Partial Oxidation of Methane, Methanol, and Mixtures of Methane and Methanol, Methane and Ethane, and Methane, Carbon Dioxide, and Carbon Monoxide

Jin-Woo Chun and Rayford G. Anthony*

Department of Chemical Engineering, Kinetics, Catalysis and Reaction Engineering Laboratory, Texas A&M University, College Station, Texas 77843

The homogeneous partial oxidation of methane involves the primary reactions of methane oxidation as well as the secondary reactions with the reaction products formaldehyde, methanol, and carbon monoxide. The complex free-radical set of reactions are modeled using a pseudo-first-order reaction parallel-series network of the three reactions methane to methanol, methane to carbon monoxide, and methanol to carbon monoxide. The secondary reaction of methanol to carbon monoxide increases as the oxygen concentration in the feed increases. For experiments with 100% oxygen conversions, increases in residence time and temperature result in further loss of methane and methanol to CO. For temperatures greater than 710 K some oxidative coupling occurs to produce ethane. The selectivity of methanol wsa 34–55% for feeds of 2.3–4.4% oxygen and 95–98% methane and 50 atm. The selectivity was highest at low conversions and low oxygen feed concentrations.

Introduction

Methanol is used as a raw material to make formaldehyde, as a solvent, as a gasoline blending agent, and as an alternate energy source. Current technology uses three stages to make methanol from methane. The first stage is the catalytic steam reforming of methane to produce synthesis gas from natural gas. This stage is highly endothermic and consumes a considerable amount of energy. The products contain carbon monoxide, carbon dioxide, and hydrogen. The second stage is a shift reactor to obtain the desired hydrogen to carbon monoxide and carbon dioxide ratio. The third stage is to produce methanol from synthesis gas. The direct oxidation of methane to methanol has potential, because it eliminates the steam reforming stage and the water gas shift reactors, and replaces the methanol reactor with a partial oxidation reactor.

Fox et al. (1988) and Edwards and Foster (1986) concluded that direct oxidation of methane to methanol would be competitive with current technology if methane conversions of 5.5% and methanol selectivities of 80% could be achieved. Brown and Parkyns (1991), Pitchai and Klier (1986), Foster (1985), and Gesser et al. (1985) published review articles describing the partial oxidation of methane to methanol. In most cases, the selectivity of methanol was too low for commercialization. However, Yarlagadda et al. (1988) have reported methanol selectivities of 75–80% at 8–10% conversions. They also reported carbon balance closures within 10%, but they did not report their closures of oxygen balances. By making a few simple assumptions, we have shown these balances to be grossly in error. Burch et al. (1989) and Helton (1991) attempted to reproduce Yarlagadda et al.'s (1988) experiments, but the high methanol selectivities at 8–10% conversions were not obtained.

Rytz and Baiker (1991) reported on experiments conducted using a flow reactor packed with 1–2-mm quartz beads with a quartz liner. The gases were preheated separately before entering the reactor where they were mixed. The schematic of their sequence system indicates temperatures were measured at the point of mixing and at the exit of the heated section, and the temperature range for the study was 425 (698 K) to 500 °C (773 K). At 723 K and above, methanol and carbon monoxide selectivities increase and ethylene selectivities decrease with increasing space time and methane conversions. They also show that space times of 3–12 s are sufficient to obtain 100% conversion of the oxygen.

A major failure of many of the earlier studies on methane oxidation was the lack of closure of the oxygen balances. In many cases the closures of the oxygen balances were not reported. Wiezevich and Frolich (1934) reported that exit products from the reactor contained only about 70% of the inlet oxygen. Boomer and Thomas (1937a,b) reported that their oxygen balance was greatly in error. They attempted to trace the oxygen discrepancy, but were unable to determine the cause of the loss of the oxygen. Helton (1991) showed that closure of the oxygen balances was necessary to ensure a minimum error in the calculated methanol selectivities. He showed that large deviations in product selectivities could occur even when the overall material and carbon atom balance closures are satisfied to within ±2%.

The objectives of this study are the following:

1. Develop an empirical kinetic model to interpret the effects of oxygen concentration, residence time, and reaction temperatures on methanol selectivities and methane conversions, and establish a base set of conditions for conducting catalytic studies (Chun and Anthony, 1993a).

2. Determine the effect on selectivities and conversions by feeding a synthetic gas mixture composed of 5% ethane and 95% methane and oxygen.

3. Determine the effect on conversion and methanol selectivities of cofeeding carbon monoxide and carbon dioxide with methane and oxygen. If the selectivity of methanol does not decrease, the cost of separation of carbon monoxide from methane may be eliminated.

4. Determine the effect of total pressure and partial pressure of methane on the reaction rate and methanol selectivities.

Experimental Methods

Reactor System. Autoclave Engineers' microscale bench-top reactor with a 900 control system was used for this study. The tubular reactor was located in a reactor

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* Address correspondence to this author.

oven. The reactor oven temperature was maintained at 423 K, and the process line from the reactor oven to the gas chromatograph (GC) was maintained above 453 K to prevent condensation of methanol and water. A 46-cm Pyrex tube inserted inside a 316 stainless steel tube was used as a reactor, and the inside diameter of the Pyrex reactor tube was 10 mm. A Pyrex tube was used as a sheath over a 316 stainless steel thermowell, and the outside diameter of the thermowell with the sheath was 6 mm. For some runs two Pyrex tubes were used as liners to decrease the inside diameter of the reaction tube from 10 to 7 mm and a thinner wall Pyrex tube was used to sheath the thermowell so that the outside diameter of the sheath was 5 mm. The volume of the reactor was decreased so that experiments could be conducted with shorter residence times. Hence, all experiments reported herein were for an empty Pyrex tube; i.e., no packing of any kind was used. The length of the heating jacket for reaction was 16.5 cm, which was divided into three heating zones. The reactants passed through a mixer/vaporizer assembler, an eight-port switching valve, and then to the fixed bed reactor. The temperatures of the furnaces for the reaction zone were 623–773 K, and pressures up to 50 atm were used. The reactor effluent flowed through a 2-μm filter, a back-pressure regulator, and the switching valve prior to exiting the reactor oven. The products were analyzed by on-line GC. An axial temperature profile was measured for each reaction condition by moving a K-type thermocouple up and down inside the thermowell. The temperature profiles were measured for feeds of methane and of methane and oxygen to the reactor. When oxygen was added to the methane feed, a difference in the temperature profiles occurred. This difference was used to determine the location of the reaction zone. A similar procedure was used to locate the reaction zone for feeds other than methane and oxygen.

Because the Reynolds numbers for this study are less than 50, laminar flow is occurring in the reactor. However, because of the short residence times, the length of the reactor, and the temperature profiles, the gas is in a dispersive flow regime. Holland and Anthony (1989) have shown that, for long reactors where the ratio of the Damköhler number to the Peclet number is less than 0.1, the plug flow assumption is a valid assumption. This ratio for this study is less than 0.01.

Chemicals. Methane from two sources, Specialty Gases and Equipment Co. and Airco, were used in this study. The methane from Specialty Gases and Equipment Co. was CP grade with the specification of 99.0% methane, 50 ppm oxygen, 2000 ppm nitrogen, 100 ppm CO_2, 50 ppm CO, 500 ppm ethane, 500 ppm ethylene, 300 ppm propane, 300 ppm propylene, 100 ppm C_{4+}, and 10 ppm H_2O. The purified methane from Airco had specifications of 99.0% methane, 0.6% nitrogen, 0.5% oxygen, 0.2% CO and CO_2, and 0.127% ethane. Oxygen with 99+% purity was purchased from Airco.

Results and Discussion

Material Balances. For the atom balances for carbon, hydrogen, and oxygen, actual flow rates were used. Therefore, when only methane and oxygen were fed, the molar flow rate of carbon fed was equal to the flow rate of methane and the molar flow rate of carbon in the exit stream was equal to $\Sigma \alpha_i n_{i,e}$ of product. The carbon balance becomes
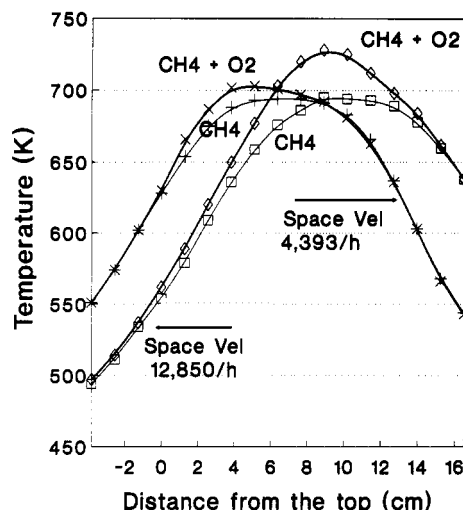

Figure 1. Axial temperature profiles with feeds of 4% O_2, 96% CH_4, and CH_4 only. (Pressure = 50 atm; heating jacket temperature = 718 K. At 4393 h^{-1} (residence time ≈ 17 s), (+) CH_4; (×) CH_4 + O_2. At 12 850 h^{-1} (residence time ≈ 8 s), (□) CH_4; (◊) CH_4 + O_2.)

$$\text{carbon balance} = \frac{\Sigma \alpha_i n_{i,e}}{\alpha_{CH_4} n_{CH_4,f}} \times 100$$

where α_i = number of carbon atoms of species i, $n_{CH_4,f}$ = molar flow rate of methane in feed, and $n_{i,e}$ = molar flow rate of species i in reactor effluent. The oxygen and hydrogen balances were calculated using the same procedure.

For 100 experiments and an oxygen feed of 4.35% with the balance being methane, the carbon balances were within 100.0 ± 0.5%, the hydrogen balances were within 100.0 ± 0.4%, and the oxygen balance was within 100 ± 6%. With a feed of 2.3% oxygen and the balance methane and seven experiments, the carbon balances were within 100.0% ± 0.3%, the hydrogen balances were within 100.0 ± 0.2%, and the oxygen balances were within 109 ± 5%. Because of the low conversions of methane, a high level of accuracy for carbon and the hydrogen balances was expected. An additional error analysis was conducted using the atom ratio of H:C on the reactor effluent, but excluding methane. This ratio was also always very close to 4; i.e., the deviation was significantly less than the deviations obtained for the oxygen balances. Errors in the atom balance on the limiting reactant, oxygen, increase by decreasing the oxygen concentration in the feed. This can be explained by Helton's (1991) sensitivity analysis. He showed that expected oxygen closures were significantly increased from 100 ± 5% to 100 ± 20%, if the oxygen feed concentration decreased from 9.4 to 2.3% and the deviation in carbon atom balance closure was 1%. These results indicate that the oxygen balance must have a minimum error to obtain reliable experimental data, even though the carbon and hydrogen balances are very accurate.

This work and Helton's (1991) statistical analysis indicate that the discrepancy of closures of oxygen balance reported by Wiezevich and Frolich (1934) and Boomer and Thomas (1937a,b) probably came from the poor analysis of product or errors in measured flow rates.

Axial Temperature Profiles. Figure 1 shows the axial temperature distribution. When the oxygen was added to the methane feed, the reactor temperature rose, and the reaction zone was considered to be the zone where the temperature profile for the methane and oxygen feed deviated from the temperature profile with a methane feed. This difference increased significantly by increasing the space velocity. To calculate the average reaction
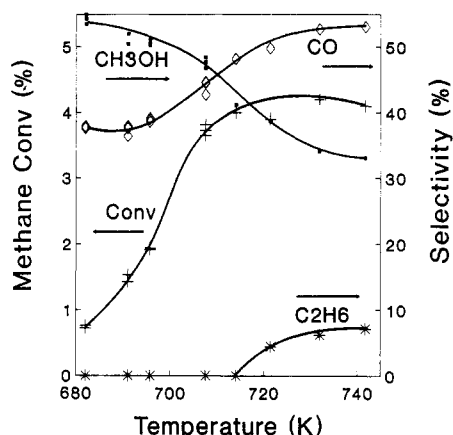
Figure 2. Effect of the reaction temperature on conversions and product selectivities for methane oxidation. (Pressure = 50 atm; residence time = 2-2.2 s; feed: 4% oxygen, 96% methane).

temperature, seven measured points were used at 1.27-cm increments. The average reaction temperature in the reaction zone was calculated as follows.

$$T_{av} = \frac{\sum_{j=1}^{N} T_i}{N}$$

where N = number of points measured in the reaction zone (seven points at 1.27-cm increments). For each run, the maximum temperature and three points above and three points below the maximum temperature were used. For the cases shown in Figure 1, the reaction zones are 1.3-8.9 cm for space velocity of 4393 h⁻¹ and 5.1-12.7 cm for space velocity of 12 850 h⁻¹. The shift in the location of the maximum temperature is an indication that the overall heat-transfer coefficient was essentially constant even with an increase in the velocity. This result is obviously due to the inability to transfer the additional energy generated by reaction; i.e., since oxygen conversion is 100% for both cases, more moles of methane reacted at high space velocity.

When the reaction occurred at residence times of 8-17 s, the oxygen conversion was 100% and methane conversion was approximately 4%. When the residence time was 2 s, low methane conversions (oxygen conversions less than 100%) were obtained. Figure 2 shows that methanol selectivities with oxygen conversions less than 100% are higher than with 100% oxygen conversions. It also shows that the kinetically significant region for methane oxidation to methanol is at oxygen conversions less than 100%. Rytz and Baiker (1991) report results opposite to these; i.e., they report methanol selectivities increase with conversions. However, as illustrated in Figure 1 and Table I, the maximum temperature observed in this study at oxygen conversions less than 100% is less than the temperature of 450-500 °C reported by Rytz and Baiker. It is also highly probable that the temperatures in the heat zone of their reactor were greater than the measured temperatures before and after the heated zone.

For average temperatures greater than 713 K, the product in our study contained ethane. By increasing the reaction temperature, ethane selectivity increased and methanol selectivity decreased. These results indicate that a small number of methyl radicals dimerized to ethane at temperatures greater than 713 K. Chun and Anthony (1993b), Chun (1992), Helton (1991), and Onsager et al. (1989) utilized free-radical models to simulate homogeneous oxidation of methane to methanol at low temper-

atures (660-730 K). Their models show that CH_4 reacts with many free-radical species to form $CH_3 \cdot$. The methyl radical was converted to $CH_3O \cdot$, $CH_3OO \cdot$, and CH_3OOH, which were subsequentially converted to CH_3OH, $HCHO$, CO, and CO_2. Their models contained the equilibrium reaction

$$CH_3 \cdot + O_2 \leftrightarrow CH_3OO \cdot$$
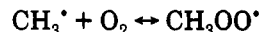
that controls production of ethane and oxygenates. Mackie (1991) estimated the concentration ratio of $CH_3OO \cdot$ to $CH_3 \cdot$ on the basis of the above equilibrium reaction. His estimation showed that high pressures (50 atm) and a reaction temperature of 723 K favors an increase of $CH_3OO \cdot$ and that low pressure (1 atm) and high reaction temperatures (1023 K) promote an increase of $CH_3 \cdot$. It is known that the principal route to ethane is through dimerization of methyl radical at high temperatures. Some ethane was produced as illustrated in Figure 2 at temperatures greater than 713 K. Therefore, data collected at temperatures greater than 713 K were not used in the development of the empirical kinetic model.

Empirical Kinetic Model. Utilizing the data from Figure 3 and subsequent data presented in Figures 4 and 5, a pseudo-first-order reaction network was developed to aid in the interpolation and interpretation of the experimental data. For simplicity and to account for an observed partial pressure effect, methane oxidation was assumed to be first order in methane. The following reaction sequence was used to calculate activation energy, because CO and CH_3OH appeared to be produced by competitive reactions.

$$CH_4 + (1/2)O_2 \rightarrow CH_3OH \quad r_1 = k_1 C_{CH_4}$$

$$CH_4 + (3/2)O_2 \rightarrow CO + 2H_2O \quad r_2 = k_2 C_{CH_4}$$
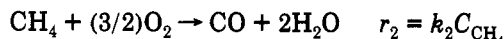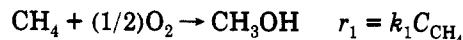
The reactor was assumed to be in plug flow, and the rate constants were assumed to follow the Arrhenius temperature dependence. Since the reactions were conducted in a nonisothermal mode, the temperature profiles and the heated zone of the reactor, 0-0.1651 m, were used in the development of the rate equations. Average temperatures and residence times were used as a convenient means of presenting the data. By assuming equal activation energies of methane to methanol and of methane to carbon monoxide, the following equations are obtained for a plug flow reactor.

$$-dn_{CH_4}/dV = (k_{10} + k_{20}) \exp((-E_1/R)(1/T - 1/T_0))C_{CH_4}$$

where

$$dV = S \, dz$$

$$C_{CH_4} = n_{CH_4}/(v_{T_0}T/T_0)$$

k_{10} and k_{20} are the rate constants at the reference temperature, $T_0 = 673$ K. Separation of variables, the use of methane conversion, and integration yield

$$-\ln(1 - X_{CH_4}) = \int_0^L S(k_{10} + k_{20}) \times$$
$$\exp((-E_1/R)(1/T - 1/T_0))/(v_{T_0}T/T_0) \, dz$$

$$Y_{EXP,i} = -\ln(1 - X_{CH_4})$$

$$Y_{CALC} = \int_0^L S(k_{10} + k_{20}) \times$$
$$\exp((-E_1/R)(1/T - 1/T_0))/(v_{T_0}T/T_0) \, dz$$

By using the measured temperature profiles and a nu-

Table I. Temperature Profiles for Experiments Presented in Figure 2[a]

L, cm	R1	R2	R3	R4	R5–R7	R8–R10	R11–R13	R14–R16
-2.54	507	504	501	499	497	495	495	494
-1.27	540	534	531	527	526	523	522	521
0	576	568	563	558	558	553	553	552
1.27	613	605	598	594	592	590	588	587
2.54	651	638	629	626	624	619	617	614
3.81	684	671	659	654	651	647	644	640
5.08	712	696	684	676	674	669	667	661
6.35	732	713	700	692	689	684	680	674
7.62	745	726	710	702	698	691	688	681
8.89	754	736	719	709	704	697	693	685
10.16	757	748	727	715	709	700	695	687
11.43	750	750	736	723	714	703	698	688
12.7	736	735	737	726	717	702	696	685
13.97	718	715	721	721	713	693	687	676
15.24	694	691	693	702	698	674	668	658
16.51	673	668	668	677	677	655	649	640
17.78				589	595	582	579	574
19.05	567	564	561	563	566	559	554	551
av T	742	732	722	714	708	696	691	682

[a] Experimental conditions are presented in Figure 2. Average temperatures and residence times were calculated by using three temperatures on each side of the maximum temperature and reactor length of 7.62 cm.
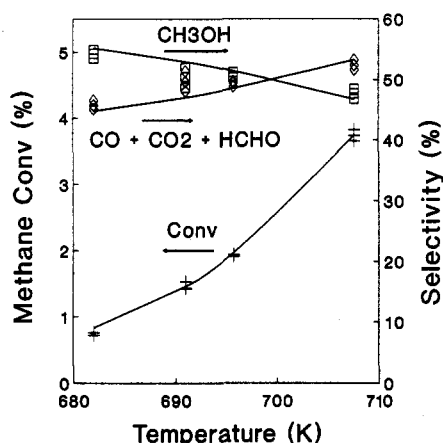

Figure 3. Comparison of model predictions with experimental data for methane oxidation at oxygen conversions less than 100%. (Pressure = 50 atm; residence time ≈ 2 s; feed: 4% oxygen, 96% methane. Solid lines, model predictions; symbols, data).

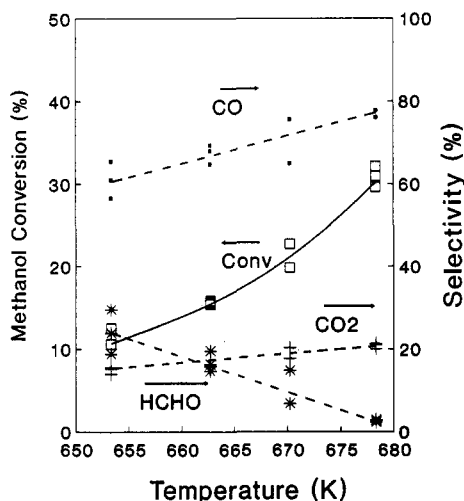**Figure 4.** Effect of reaction temperature for methanol oxidation. (Pressure = 50 atm; residence time ≈ 14.2 s; feed: 6% oxygen, 14% methanol, 80% helium. Solid line, simulation; symbols and dotted lines, data and smooth curves.) [Note: The model predicts combined CO, CO2, and HCHO selectivities.]

merical method for evaluating the integral, nonlinear parameter estimation can be used to determine the activation energy and the sum of $k_{10} + k_{20}$. A Gauss–Legendre quadrature (Burden et al., 1981) with 24 points
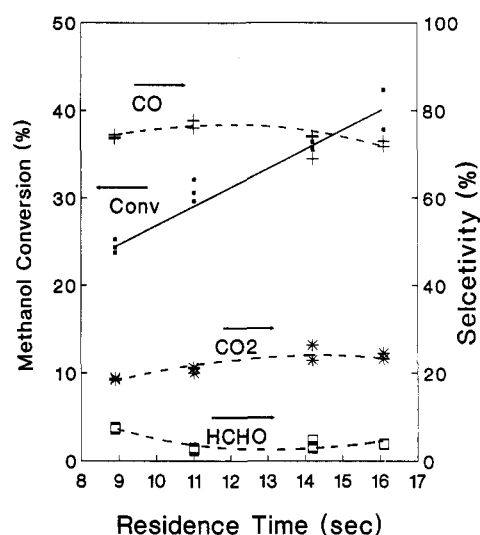

Figure 5. Effect of residence time for methanol oxidation. (Temperature = 678 K; pressure = 50 atm; feed ratio of CH3OH:O2 ≈ 2.37:1. Flow rate of He was changed in order to vary residence times. Partial pressure of helium varied from 35.3 to 41.9 atm. Solid line, simulation; symbols and dotted lines, data and smooth curves.) [Note: The model predicts combined CO, CO2, and HCHO selectivities.]

was used to evaluate the integral, and the value of F defined below was minimized.

$$F = \sum_{i=1}^{n} (Y_{EXP,i} - Y_{CALC,i})^2$$

The rate constant at 673 K and the activation energy for methane partial oxidation were determined by using the data presented in Figure 2 and Table I for methane conversions less than 4%, which correspond to oxygen conversion less than 100%. The values for $k_{10} + k_{20}$ and E_1 were 6.17 h^{-1} and 233 760 J/mol, respectively. This value of the activation energy is close to the value of 238 260 J/mol reported by Tsang and Hampson (1986) for abstraction of the hydrogen atom from methane by molecular oxygen, that is,

$$CH_4 + O_2 \rightarrow CH_3{}^{\bullet} + HO_2{}^{\bullet}$$
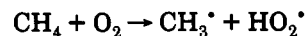
Kinetics of the Partial Oxidation of Methanol. Since the secondary reactions for oxidation of methanol are obviously occurring, a study of partial oxidation of
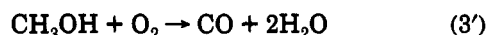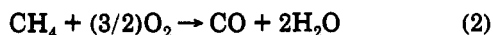
methanol was conducted using the empty Pyrex tube reactor. Methanol, oxygen, and helium were used as the feeds. The oxygen and methanol feeds of 4.8–8.7% oxygen and 11.4–20.7% methanol with the balance being helium were used for the kinetic studies. Without oxygen and at 50 atm, methanol in helium did not decompose at temperatures less than 773 K. When oxygen was added to the feed, the methanol was oxidized to carbon monoxide, carbon dioxide, formaldehyde, and water with the main product being carbon monoxide. Because the reaction is exothermic, when the oxygen was added to the feed the temperature rose. The reaction zone was considered to be the region where the temperatures with and without oxygen feed were different. The reaction temperature was calculated by averaging the temperatures in the reaction zone. Figure 4 shows that conversions of methanol increased and the selectivity of carbon monoxide increased by increasing the reaction temperature. Figure 5 shows that by increasing the residence time the methanol conversion increased, but carbon monoxide selectivity was essentially constant. Oxygen conversions varied from 58 to 89%. For the experiments reported in Figure 5, the temperature profile with the reactor for each experiment was maintained essentially the same by adjusting the heating jacket temperatures.

By using the plug flow assumption, the measured temperature profiles, and the methanol conversions a pseudo-first-order rate equation was found to fit the data, i.e, $r_3 = k_3 C_{CH_3OH}$. The same procedure as described above was used to determine the values of the rate constant at 673 K and the activation energy, which were 138.32 h^{-1} and 186 090 J/mol, respectively. This value of the activation energy is close to the value, 188 090 J/mol, reported by Tsang and Hampson (1986) for hydrogen atom abstraction. The hydrogen abstraction reaction is as follows:

$$CH_3OH + O_2 \rightarrow CH_2OH^{\bullet} + HO_2^{\bullet}$$
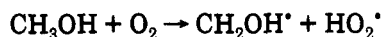
Burch et al. (1989) concluded that methanol in a Pyrex-lined reactor was remarkably stable, and there was virtually no partial oxidation of methanol with oxygen, even at 773 K. A mixture of methanol and oxygen was used, and it is not clear if they used inert gas for dilution. Their result differs from this work. Bone et al. (1935) found that methanol was oxidized much faster than methane when using a silica reactor at 1 atm, and the main product was carbon monoxide. Even though they did their experiment with a batch reactor at 1 atm, the carbon monoxide selectivities of 78–85% were similar to our results.

Combined Reaction Model. To predict methane conversion, methanol selectivities, and lumped (CO$_x$ and HCHO) selectivities, the methane and methanol oxidation reactions were combined to obtain the following reaction sequence:

$$CH_4 + (1/2)O_2 \rightarrow CH_3OH \tag{1}$$

$$CH_4 + (3/2)O_2 \rightarrow CO + 2H_2O \tag{2}$$

$$CH_3OH + aO_2 \rightarrow bCO + cHCHO + dCO_2 + eH_2O \tag{3}$$

$$CH_3OH + O_2 \rightarrow CO + 2H_2O \tag{3'}$$

To obtain a value for k_{20}, the difference in (CO$_x$ + HCHO) production and (CO$_x$ + HCHO) production predicted by reaction 3' was attributed to reaction 2. A value of 2.466 h^{-1} was obtained. The rate constants and activation
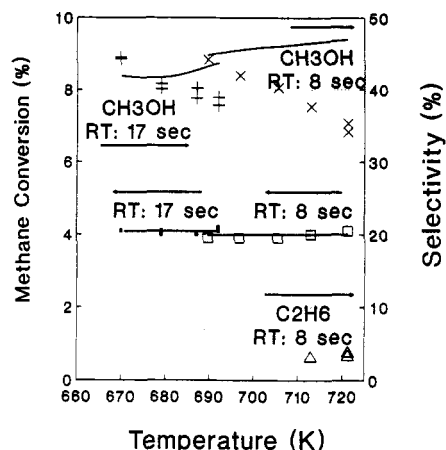

Figure 6. Effect of temperature and residence time on methanol selectivities and methane conversions for 100% oxygen conversions. (Pressure = 50 atm; feed: 4% oxygen, 96% methane. Solid lines, model predictions; symbols, data.)
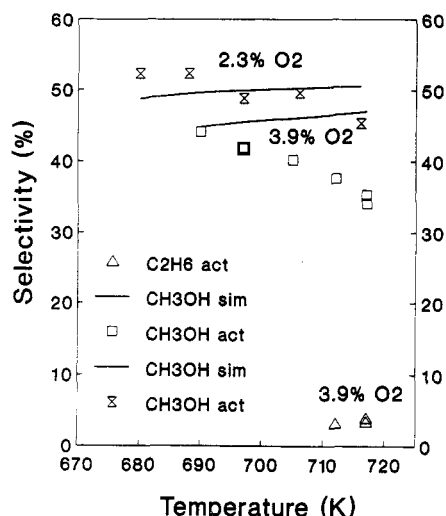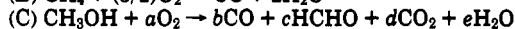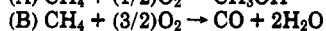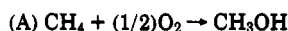

Figure 7. Effect of oxygen concentrations on methanol selectivities. (Pressure = 50 atm; oxygen conversion = 100%; residence time ≈ 8 s. Solid lines, model simulation; symbols, data).

Table II. Activation Energy and Rate Constant with Empty Pyrex Tube (Pressure = 50 atm)

reaction	rate expression	I	k_{I0}(673 K) (h^{-1})	E_I (J/mol)
A	$r_{CH_4,1} = k_1 C_{CH_4}$	1	3.704	233 760
B	$r_{CH_4,2} = k_2 C_{CH_4}$	2	2.466	233 760
C	$r_{CH_3OH,3} = k_3 C_{CH_3OH}$	3	138.32	186 090

(A) $CH_4 + (1/2)O_2 \rightarrow CH_3OH$
(B) $CH_4 + (3/2)O_2 \rightarrow CO + 2H_2O$
(C) $CH_3OH + aO_2 \rightarrow bCO + cHCHO + dCO_2 + eH_2O$

energies for these reactions are summarized in Table II. For temperatures less than 710 K and oxygen and methane conversions less than 100 and 4%, the calculated curves for methane conversion, methanol selectivity, and methanol conversion match the experimental data very well as illustrated in Figures 3–5.

Figures 6 and 7 show that the kinetic model predicted the methane conversions reasonably well. The model indicated that oxygen was consumed within 2 s after entering the reactor for both sets of residence times, and that the selectivity of methanol decreases from the top of the reactor to the bottom of the reactor because of the oxidation of methanol to carbon oxides. Considering the fact that the model predicts that all of the oxygen was consumed in the first 2 s in the reaction zone, the model does a fairly good job of predicting methanol selectivity
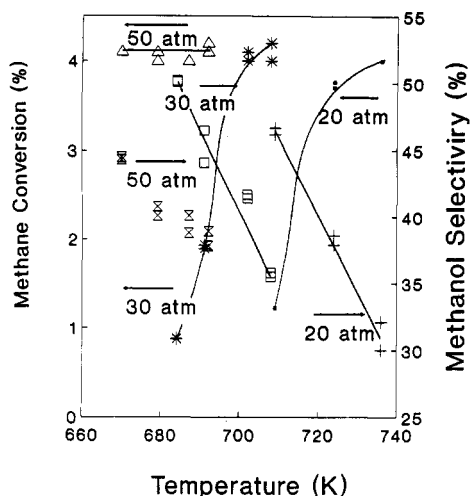
Figure 8. Effect of reaction pressure for methane oxidation. (Space velocity, 4493 h^{-1}; feed: 4% oxygen, 96% methane.)
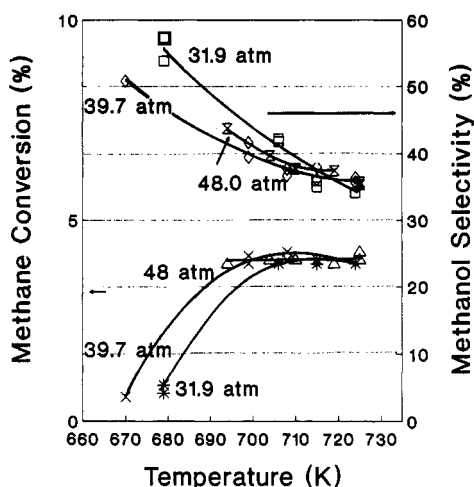

Figure 9. Effect of inert feed (nitrogen) for methane oxidation. (Total pressure = 50 atm; residence time ≈ 6 s; feed ratio of CH$_4$:O$_2$ = 1.00:0.04. Pressures are partial pressure of methane.)

of the first point for each residence time. Obviously, the model overpredicts methanol selectivities for the remaining points at the higher temperatures for each residence time. Several possibilities exist for the failure of the model to predict the decrease in methanol selectivities as the temperature increases for each space velocity. These are stated as follows:

(a) For each residence time the experiments were conducted by starting at a low furnace temperature and gradually increasing the temperature in 10-deg increments until reaction occurred. This procedure, as illustrated in Figures 8 and 9, usually resulted in almost no methane conversion and a small oxygen conversion followed by a significant increase in the reaction temperature, which resulted in a methane conversion of about 4.3% and an oxygen conversion of 100%. For a residence time of 17 s this step change occurred at an average temperature of about 670 K. This average temperature is less than the lowest average temperature used in developing the empirical model. Because of the empirical nature of the model compared with the complexity of the set of free-radical reactions, the model failed to predict the higher methanol selectivity for the first point.

(b) When the residence time was maintained essentially constant at 17 s, and the temperature was increased, more CO was produced, and methanol selectivity decreased. The model fails to predict this decrease because the activation

energy for producing CO is probably greater than the activation energy for producing methanol. The dehydrogenation reaction was not included in the model because the experiments with methanol and helium feeds showed no loss of methanol by dehydrogenation up to 773 K. Again the model was developed for the range of conditions which result in 20–100% oxygen conversions. Since the model predicts that 100% of the oxygen is consumed within the first 2 s after entering the reactor, only a small amount of methanol is lost after all of the oxygen is consumed. This phenomenon was observed by Rytz and Baiker (1991) and Burch et al. (1989).

Figure 7 shows the selectivity of methanol decreased with increased oxygen in the feed. The loss of methanol is apparently due to the secondary reactions of oxidation of methanol to carbon monoxide.

Effect of Pressure. For a constant feed rate Figure 8 shows that as the reactor pressure is decreased the reaction rate decreases as indicated by the need to increase the temperatures to obtain significant conversions of oxygen. The empirical model predicts the decrease in the reaction rates, but to predict conversions in the range of the experimental data, the activation energy was increased from 233 760 J/mol obtained at 50 atm to 290 940 J/mol for the 30-atm data. Because of the reduction in reaction rate at 30 and 20 atm, oxygen conversions less than 100% are readily obtained at constant feed rates by changing the reaction temperature. The selectivities of methanol decrease with increasing temperatures and oxygen conversions at pressures of 20 and 30 atm in the same manner as at 50 atm. However, because of the higher temperatures required when the same feed rate is used, the methanol selectivities at 100% oxygen conversion are less than those at 50 atm. Simulations using the empirical kinetic model also show the decrease in methanol selectivities with increasing oxygen conversion because of the secondary reactions of methanol conversion to carbon oxides.

Effect of Inert Feed. A comparison of methane conversions presented in Figure 8 with those presented in Figure 9 illustrates that the effect of total pressure for methane–oxygen feeds is primarily a methane partial pressure effect, but methanol selectivities are approximately the same for the methane–nitrogen–oxygen feeds and the methane–oxygen feed. The fact that reducing the partial pressure of methane and oxygen with nitrogen affects only the conversion, but does not affect the selectivity of methanol, illustrates the complexity of the mechanism for methane oxidation.

Effect of Ethane Feed. As illustrated in Figure 10, when a feed of methane–ethane–oxygen was used, the conversion of ethane was about 21% (half of the carbon conversion) and the selectivity of ethylene was 3.5–6.4%. The reaction temperature to obtain 100% oxygen conversion also decreases, and the selectivity of methanol decreases. Since all of the experiments in Figure 10 are for 100% oxygen conversion, a continued increase in temperature results in a continuous decrease in the methanol selectivity, which is probably due to the increase in the secondary reactions at the higher temperatures. Burch et al. (1989) and Helton (1991) also showed that reaction temperatures with additives were lower than that with the methane feed and oxygen feeds. They also showed that the selectivities of methanol based on total carbon compounds fed did not change with the mixed feed. This work shows a slight decrease in the methanol selectivity based on the total carbon compounds fed. However, further work is needed because this work as well as that of Burch and Helton were for 100% oxygen conversions,
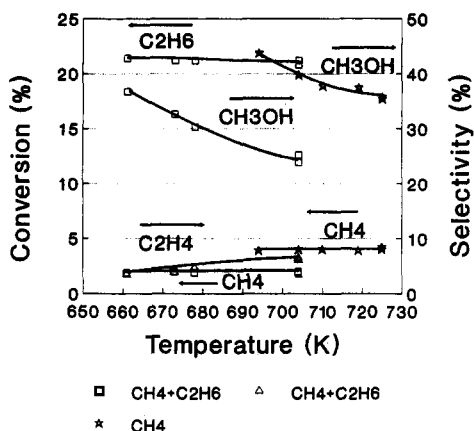
Figure 10. Comparison of conversions and selectivities for oxidation of methane (4% oxygen, 96% methane; pressure = 50 atm, residence time ≈ 6 s) and oxidation of a mixture of methane and ethane (feed: 90.7%, methane, 5.3% ethane, 4.0% oxygen; pressure = 50 atm; residence time = 6 s).
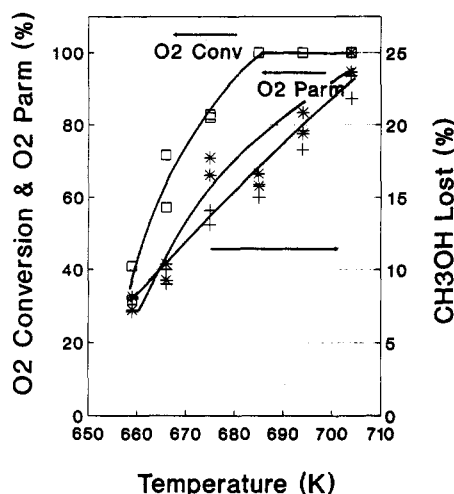

Figure 11. Oxidation of a mixture of methane and methanol. (Residence time ≈ 15 s; feed: 81% methane, 3.7% oxygen, 15.3% methanol; pressure = 50 atm.)

and this study clearly shows that if oxygen conversions are 100% a variety of results can be obtained depending upon the flow rates and temperatures.

Oxidation of Mixtures of Methane and Methanol. To substantiate the methodology used in developing the empirical kinetic model for oxidations of methane–oxygen mixtures, a feed composed of 81% methane, 3.7% oxygen, and 15.3% methanol was fed to the reactor. To separate the carbon oxides produced by methanol from the oxidation of methane, an O_2 Parm index was defined as the oxygen needed (by calculation) when methanol was oxidized to carbon monoxide, carbon dioxide, formaldehyde, and water divided by oxygen consumption obtained from the experiment. If methanol is consumed, the O_2 Parm index is 100%. If methanol and methane are oxidized together, the O_2 Parm is less than 100%. Figure 11 shows that the amount of methanol lost by secondary reaction increased by increasing the temperature. The O_2 Parm is between 30 and 70% for oxygen conversions less than 100%, and increases to 95 for temperatures greater than 694 K. This substantiates the use of reaction 3 in the kinetic model. However, Burch et al. (1989) reported that the loss of methanol due to the secondary reaction of methanol oxidation was negligible at temperatures less than 723 K, and was 15–18% at temperatures higher than 723 K. They used a saturator to feed the methanol with methane and oxygen, and the methanol
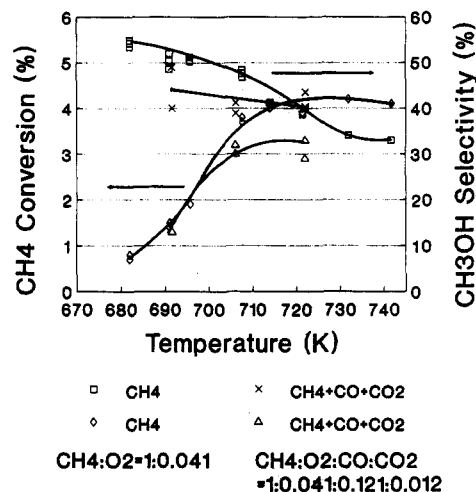

Figure 12. Comparison of methanol selectivities and methane conversions for oxidation of methane and oxidation of a mixture of methane and carbon monoxide. (Residence time ≈ 2 s; pressure = 50 atm.)

concentration of the feed was less than 1%. With a feed of 1% methanol it would be difficult to separate the loss of the methanol fed from the methanol produced by reaction and the subsequent loss of this methanol by secondary reactions. Since Burch et al. (1989) did not detect methanol loss by reaction at temperatures less than 723 K and since they did detect the loss above 723 K, they concluded the loss of methanol was unimportant for methane oxidation at temperatures less than 723 K. However, this work clearly shows the loss of methanol by further oxidation was important.

Oxidation of Mixtures of Methane, Carbon Monoxide, and Carbon Dioxide. To determine the effect of cofeeding methane–carbon dioxide–carbon monoxide and oxygen on selectivities and conversions, several experiments were conducted. The selectivity of methanol for mixed gas oxidation was defined by assuming that the methanol is only produced from methane. A comparison of Figure 12 with Figures 8 and 9 indicates that methanol selectivities for feeds of methane–carbon monoxide–carbon dioxide–oxygen are less than those obtained for methane–oxygen or methane–nitrogen–oxygen feed for oxygen conversions less than 100%; i.e., methane conversions become constant at 100% oxygen conversion. But at oxygen conversions of 100%, methanol selectivities become the same. The ratio of the moles of CO_2 produced to the mole of methane reacted varied from 37 to 58% for the mixed gas feed, but with a methane–oxygen feed carbon dioxide selectivity was less than 10%. This result indicates that the carbon dioxide was produced from carbon monoxide. The differences observed in methanol selectivities for the various cases discussed may be due to generation of additional free radicals from the CO oxidation. These free radicals would represent an increase in the number of free radicals that could interact with the methanol or with radicals that produce methanol thereby reducing methanol selectivities.

Conclusions

This study presents new data on the partial oxidation of methane and mixtures of methane with the reaction products. An empirical kinetic model was developed, which can be used as an aid in interpolating and interpreting the data and in simulation of possible reaction conditions for maximizing methanol selectivities. The model and the experimental data illustrate the decrease

in methanol selectivities with increasing oxygen feed concentrations and increasing temperature. The data and the model show that carbon monoxide is produced from methane and methanol. The kinetic model predicts reasonable values for methane conversions and product selectivities. For constant residence times and temperatures greater than that required to obtain 100% oxygen conversions, the data illustrate the decrease in methanol selectivities and free radical coupling reactions to produce ethane. At temperatures less than 700 K and residence times of 8 and 17 s, the model and data illustrate a minimum decrease of methanol selectivities even though the oxygen was obviously consumed within the first 2 s of entering the reactor.

With 100% oxygen conversion, the methanol selectivities decreased by decreasing the total reaction pressure, but the dilution of the feed with nitrogen or carbon monoxide and carbon dioxide at the same total reaction pressure did not affect the selectivity of methanol. When 5.34% ethane was added to the methane feed, the conversion of ethane was about 21% (half of the carbon conversion), and the selectivity of ethylene was 3.5–6.4%. The reaction temperature decreased for 100% oxygen conversions when ethane was added to the feed, and the selectivities of methanol decreased significantly.

Acknowledgment

Nomenclature

C_i = concentration of component i
E_I = activation energy for reaction path I
k_i = rate constant for reaction path I
K_{i0} = rate constant for reaction path I at reference temperature
L = reactor length
N = number of measuring point in the reaction zone
n_i = molar flow rate of species i
$n_{i,e}$ = molar flow rate of species i in reactor effluent
$n_{i,f}$ = molar flow rate of species i in feed
S = cross-sectional area of the reactor
T = reaction temperature
T_{av} = average temperature in the reaction zone
T_i = reaction temperature at each location of reactor
T_0 = reference temperature (673 K)
V = reactor volume
v_{T_0} = volumetric flow rate at reference pressure (50 atm) and reference temperature (673 K)
X_i = conversion of species i

Greek Letter

α_i = number of carbon atoms of species i

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