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Oxygenate Formation from n-Butane Oxidation at Short Contact Times: Different Gauze Sizes and Multiple Steady States[1]

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The production of olefins and oxygenates by partial oxidation of n-butane over a single layer of Pt–10% Rh gauze has been examined at atmospheric pressure in the fuel rich regime and in the space velocity range of 3.3×10^6 to 1.6×10^7 h^{-1} (contact times of ~1000 to 200 μs) using a single gauze reactor. We show that there is an optimum regime of space velocities to maximize the oxygenate selectivity and that at least 75% selectivity to olefins and oxygenates can be obtained. Nitrogen diluent in the feed lowers the production of oxygenates, and coarser mesh gauze gives higher oxygenate yield than finer mesh. In addition, at a specific range of fuel/oxygen feed ratios, multiple steady states are observed on the more open gauze. Analysis of the product distribution of these steady states indicates that initially the exothermic complete combustion of the butane on the gauze surface to CO_2 and H_2O provides most of the necessary heat for this process. Oxygenates and olefins are then produced by homogeneous reaction in the quench zone downstream of the gauze. A detailed model of homogeneous chemistry confirms that oxygenates are produced by homogeneous reactions.

1. INTRODUCTION

Direct production of oxygenated compounds from alkanes could have large impact on their manufacture compared to multistage processes. The current production methods of these oxygenates require multiple stages, expensive catalysts, large residence times, and careful temperature control (1, 2). In this work, we further investigate the operation of a single gauze reactor in which oxygenates such as acetaldehyde, formaldehyde, and methanol are produced from n-butane.

Previously, Goetsch *et al*. reported that oxygenates and olefins can be produced from n-butane in a one-step process, using a single woven Pt–10% Rh gauze reactor with 90 μm wire diameter and with contact times in the order of ~250 μs. The temperature of the gauze wires was measured with a pyrometer and found to be ~800°C (3, 4). Similar gauzes are currently used for the production of NO (Ostwald process) and HCN (Andrussow process) in multiple layer packs (1, 2). Replacing the n-butane with methane, ethane, propane, or isobutane resulted in negligible oxygenates production. This suggested that the primary mechanism for oxygenates production is a homogeneous intramolecular rearrangement of butyl-peroxy radicals which are expected to form in abundance immediately after the gauze (5, 6, 11). Oxygenates were also negligible when the single gauze was replaced by a five-gauze pack. A 40% maximum selectivity to oxygenates and 30% selectivity to olefins at a 10% n-butane conversion was reported.

The single gauze reactor has been the only monolithic reactor which gave significant production of oxygenates from n-butane at such high flow rates. Huff *et al*. (7–9) reported negligible oxygenates production from ethane, propane, n-butane, and isobutane partial oxidation over Pt-coated α-Al_2O_3 foam monoliths. It was suggested (3, 4) that the large transparency of the single gauze reactor allows the rapid mixing of the cold gases which bypass the gauze with the hot gases that leave the gauze surface, resulting in rapid quenching which prevents oxygenates from decomposing or combusting.

The objective of this work is to further investigate this process, find the operating parameters which lead to yield maximization, and examine the mechanisms involved in more detail.

2. EXPERIMENTAL

The reactor used in these experiments was a quartz tube 19-mm ID and 40-cm long. Two 1-cm long quartz sleeves with 17-mm OD and 15-mm ID hold the gauze between them inside the tube. The sleeves are wrapped with thin alumina cloth to prevent bypassing of gases and to ensure rigidity. The tube is wrapped with a thick insulation layer to minimize heat losses. Five mm after the gauze, a chromel–alumel thermocouple inside a quartz thermowell is used to measure the temperature at the reactor exit.

In experiments where feed preheat is needed, a region of the tube before the catalyst is wrapped with a heating tape.

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The composition and flow rates of the gases entering the system are controlled using mass flow controllers.

The catalyst was a Pt–10% Rh woven gauze with 90-μm wire diameter and either 80 mesh (~320-μm spacing) or 40 mesh (~630-μm spacing) with a purity of 99.9%. All data were reproduced on several samples with results consistent with those shown.

Reaction products are analyzed with an HP 6890 gas chromatograph, using a capillary column with a TCD detector. The carbon and hydrogen balances typically closed to within ±3%.

3. RESULTS

3.1. 80 Mesh Gauze

Initial experiments were done using 80 mesh gauze with 2.5 SLPM (standard liters per minute) feed flow rate with no preheat or nitrogen present. The n-butane/oxygen feed ratio was varied from 2 to 3.5. These results are shown in Fig. 1.

Clearly, three operating regimes are identified. In the first, for n-C_4/O_2 ratio ≤2.1, n-butane conversion exhibits its highest values. Oxygen conversion is also high (≥80%). For this regime, the major products are primarily olefins and then oxygenates. This is not surprising since the exit gas temperature is high and results in the formation of olefins which come from dehydrogenation, cracking, or oxygenate decomposition (5). The olefins produced are mainly 1-C_4H_8 and smaller amounts of 2-C_4H_8, C_3H_6, and C_2H_4. The combined $CO + CO_2$ selectivity in this regime is around 30%.

In the second regime, for n-C_4/O_2 ratio between 2.3 and 3.0, n-butane conversion decreases from ~16 to ~11%. Oxygen conversion is between ~80 and ~90%. Now, the main products are primarily oxygenates and then olefins because as n-C_4/O_2 increases, the lower temperature allows the survival of the oxygenate compounds resulting in selectivities of ~40%. The combined $CO + CO_2$ selectivity in this regime does not exceed 30%.

In the third regime, a further increase of the n-C_4/O_2 ratio beyond 3.0 causes a dramatic reduction of conversions and olefin and oxygenate selectivities, with n-butane conversion dropping to ~5% and oxygen conversion decreasing to ~60%. This sharp change appeared reversible with respect to n-C_4/O_2 feed variation. In this regime, negligible olefins

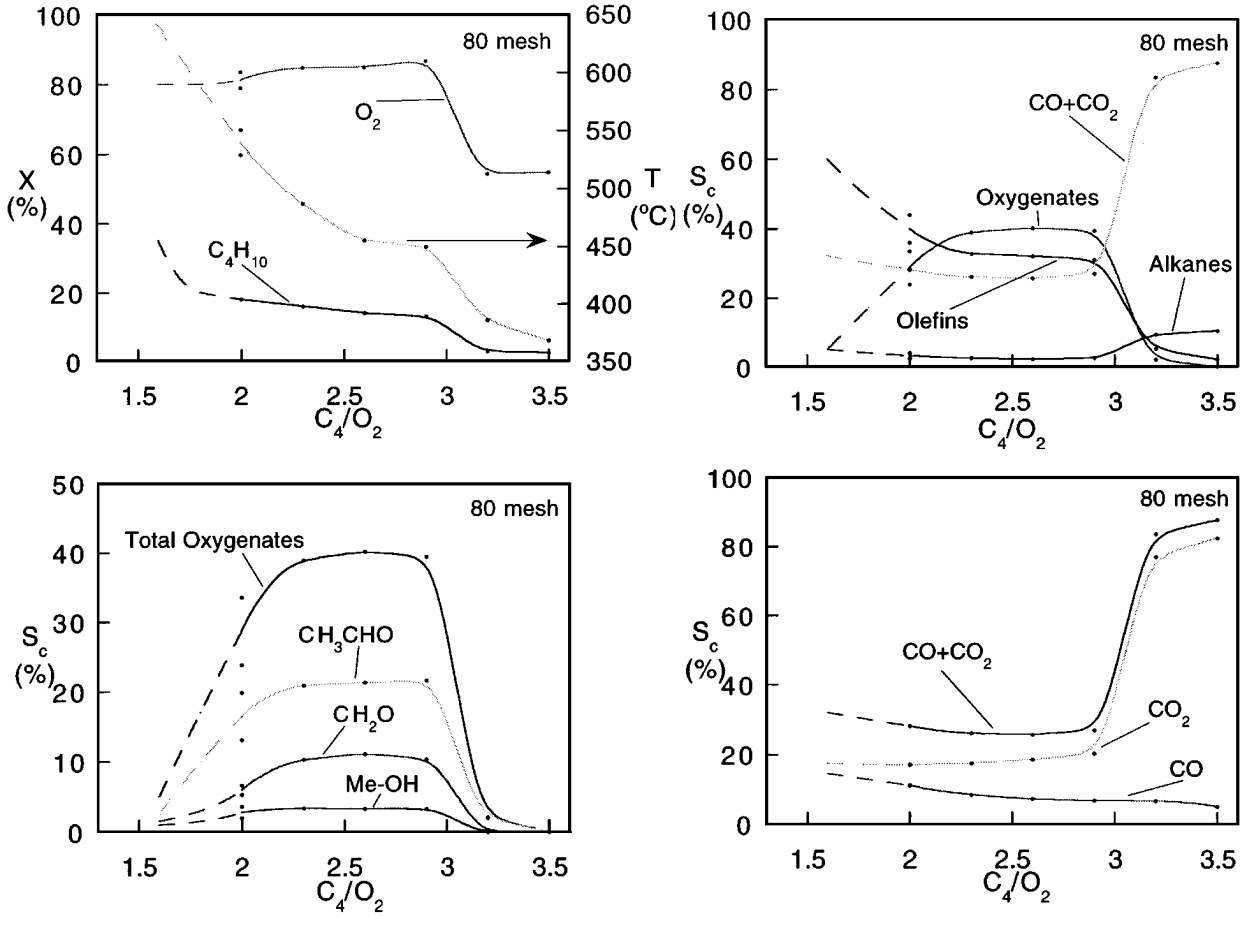

FIG. 1. Fuel and oxygen conversions, temperature, and product selectivities for a single 80-mesh Pt–10% Rh gauze reactor over a range of C_4/O_2 feed ratios. Flow rate is 2.5 SLPM; no N_2 diluent is present in the feed; no preheat.

and oxygenates are produced, whereas the main products are $CO + CO_2$. Some stable alkanes such as isobutane and neopentane remain in the product stream, and this results in an apparent increase of alkane selectivity. The main characteristics of these two regimes (high or low conversions of the feed and large or small selectivities to valuable products) will from now be used to characterize a reactor operation stage as "fully ignited" or "heterogeneous only."

All of these results are in general agreement with those reported, although we see the dominant oxygenate to be acetaldehyde, instead of formaldehyde, and oxygenate selectivity to maximize at lower n-C_4/O_2 feed ratios with slightly higher n-butane conversion (3, 4).

3.2. N_2 Dilution

To determine the effect of nitrogen dilution in the feed, experiments were made for a flow rate of 2.5 SLPM and a constant n-C_4/O_2 feed ratio of 2.6. The results are shown in Fig. 2. As expected, increasing nitrogen dilution resulted in lower n-butane and oxygen conversions, while the exit gas temperature remained almost constant which is a counterintuitive result. However, the product distribution was dramatically different between low and high dilution runs. Low nitrogen dilution (<15% in the feed) maximized selectivity of oxygenates and olefins. Further increase of dilution to values larger than 20% in the feed, resulted in minimum amounts of oxygenates and olefins, while combustion products ($CO + CO_2$) dominate in this regime. There is a clear trend in the results which indicates that to maximize the oxygenates and the olefins yield, nitrogen dilution should be as low as possible.

3.3. Flow Rate Variation

Flow rate effects are equally important in such a process. The window for optimal operation was monitored by varying the flow rate from 2 to 4 SLPM (contact times ranging from 480 to 230 μs) while keeping the n-C_4/O_2 ratio at 2.6 and introducing no nitrogen dilution in the feed. The results are shown in Fig. 3. Three operating regimes are identified.

For low flow rates, $CO + CO_2$ are the dominant products, olefins are the second largest group, and oxygenates are below 10%. Temperature has the highest values throughout the whole flow rate operating regime (~500°C) and fuel and oxygen conversions are about 7 and 75%, respectively.

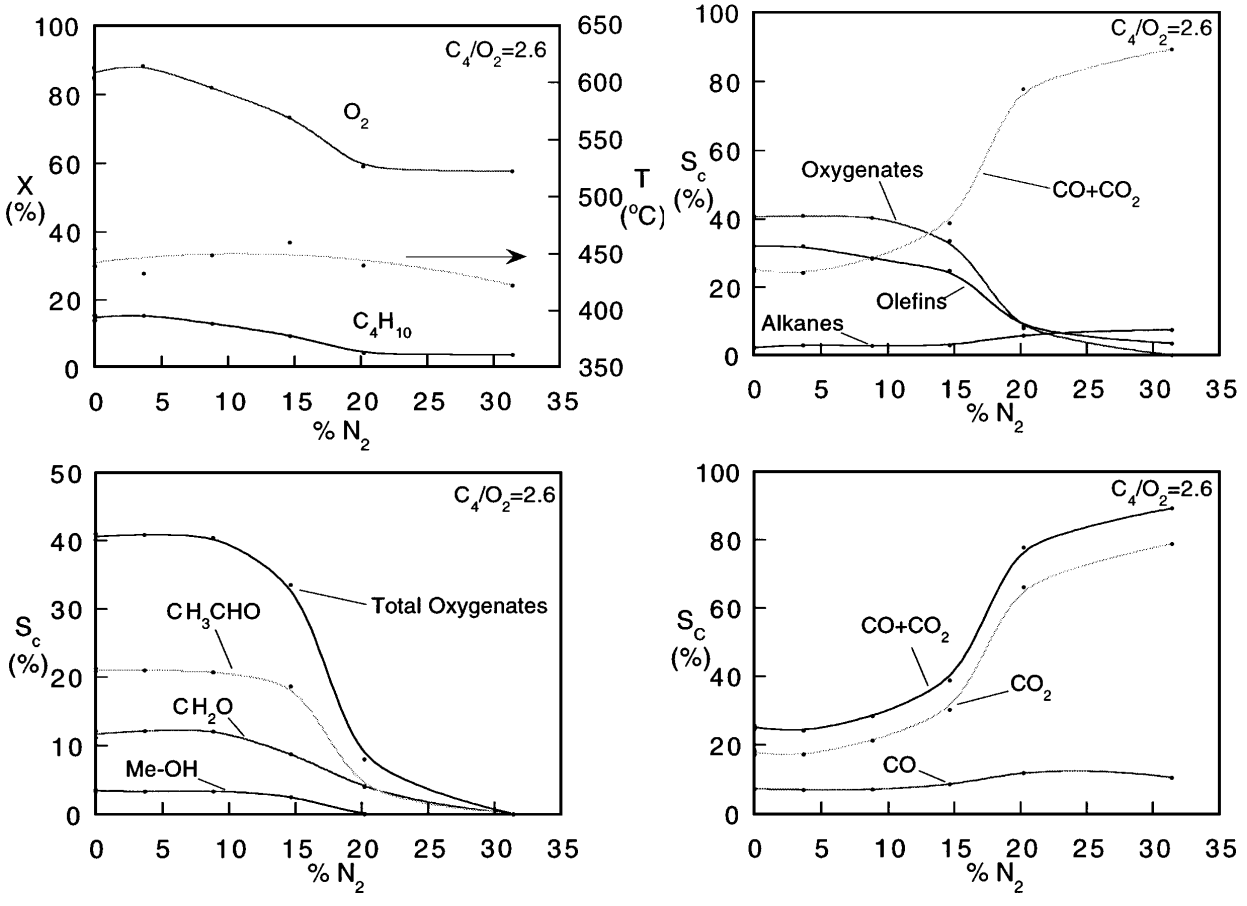

FIG. 2. Fuel and oxygen conversions, temperature, and product selectivities for a single 80-mesh Pt–10% Rh gauze reactor over a range of N_2 percentage in the feed. Flow rate is 2.5 SLPM; C_4/O_2 feed ratio is 2.6; no preheat.

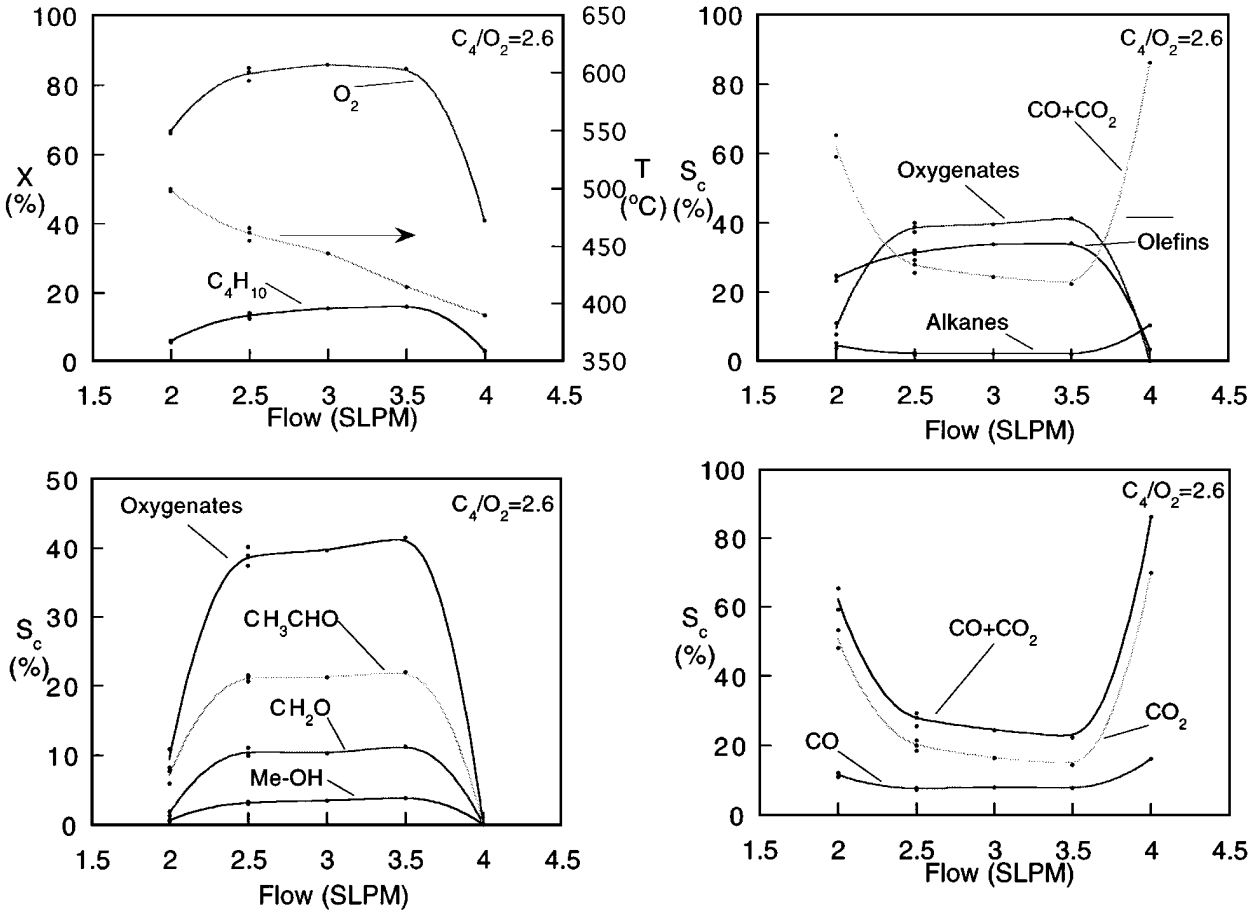

FIG. 3. Fuel and oxygen conversions, temperature, and product selectivities for a single 80-mesh Pt–10% Rh gauze reactor over a range of feed flow rates. C_4/O_2 feed ratio is 2.6; no N_2 diluent is present in the feed; no preheat.

For flow rates varying from 2.5 to 3.5 SLPM, oxygenate products maximize. Olefins are the second largest product group and combustion products are between 20 and 30%. Fuel and oxygen conversion maximize, while temperature ranges from ∼470 to ∼420°C.

Finally, for high flow rates, $CO + CO_2$ dominate again in the product stream. Oxygenates, olefins, temperature, fuel, and oxygen conversions are also minimized. At this stage, the reactor is practically "blown out" and combustion reactions on the catalytic surface dominate.

3.4. Preheat Variation

In contrast to many similar processes, the single gauze reactor we have described operates with no preheat or heat exchange. Since the process is believed to operate with a heterogeneously initiated homogeneous mechanism, the effect of preheat was examined, and the results are shown in Fig. 4. Preheat variation up to 250°C results in rise of the exit gas temperature to values from ∼450 to ∼600°C.

At these temperatures, oxygenate compounds are less likely to survive, and indeed the experiment shows a dramatic decrease of oxygenates from ∼37 to ∼10%. At higher temperatures, decomposition of aldehydes is more likely to take place through decarbonylation, and this is presumably what is happening in this experiment.

For a preheat of 250°C, olefin selectivity rises to values of ∼60%. The majority of the olefins is cracked (∼30% propylene and ∼20% ethylene). This is different from the results of experiments where no or little preheat was used. There, the dominant olefins were 1-butene (∼20% selectivity) and 2-butene (∼7% selectivity). For this high preheat, n-butane and oxygen conversion also rises to ∼30 and ∼95%, respectively.

3.5. 40 Mesh Pt–10% Rh Gauze

A parameter which has not been examined previously is the effect of the gauze mesh size. It was suggested (3, 4) that the key issue in the single gauze reactor is the rapid quenching which occurs when cold unreacted gases mix quickly with the hot gases that leave the gauze surface. The gauzes used in the experiments reported in this work were 80 mesh with a nominal transparency of 58%. The proposed mechanism indicated that a significant mesh size variation might influence the results considerably.

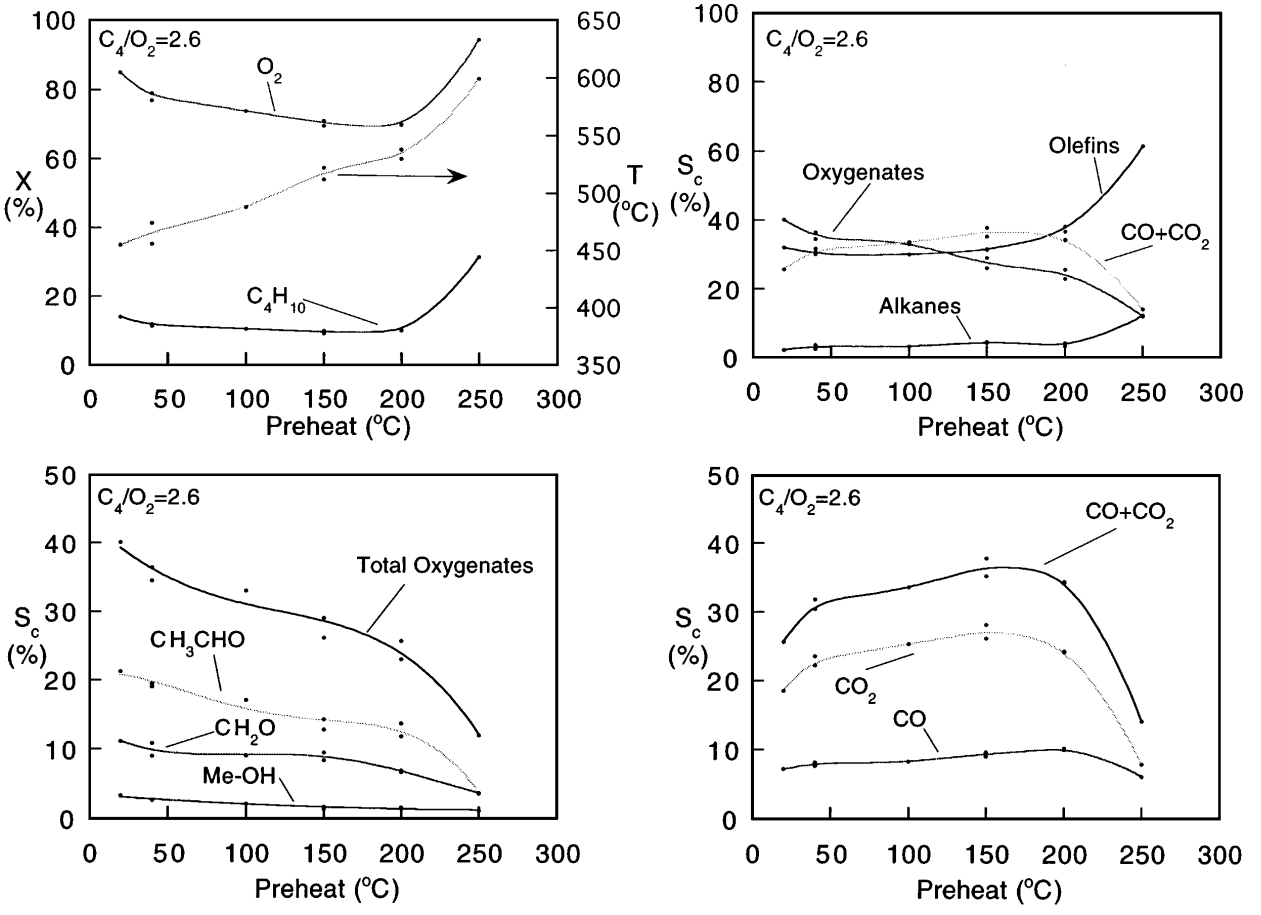

FIG. 4. Fuel and oxygen conversions, temperature, and product selectivities for a single 80-mesh Pt–10% Rh gauze reactor over a range of feed preheat temperatures. Flow rate is 2.5 SLPM; C_4/O_2 feed ratio is 2.6; no N_2 diluent is present in the feed.

We performed the same type of experiments with a single 40 mesh Pt–10% Rh gauze (77% nominal transparent) as the reactor, and the results are shown in Fig. 5. The most important feature is that the more open gauze shows higher oxygenate selectivity even with leaner operation (the n-C_4/O_2 ratio varied from 1.4 to 2.4 in the coarser gauze experiments instead of 2.0 to 3.5 in the finer gauze) with higher n-butane conversions. At the same time, the exit gas temperature remained between 300 and 450°C. This again prevented the decomposition of the oxygenate products, resulting in a total oxygenate selectivity higher than 40%. The oxygenate product distribution is almost the same for both gauze reactors, with the 40 mesh oxygenate selectivities being higher than the 80 mesh for each oxygenate product, resulting in an overall increase of the total oxygenate selectivity and yield.

For a small regime of n-C_4/O_2 feed ratios (between 2.0 and 2.3) two stable steady states were observed, which were reproduced on several gauzes. At the "fully ignited" steady states, oxygen and fuel conversions are high, whereas at the "heterogeneous only" steady states they drop significantly. Oxygenates are formed only in the "fully ignited" steady state. In the "heterogeneous only" steady state, olefin production is reduced dramatically and $CO + CO_2$ are the main products. An important observation is that the CO_2 yields of both the fully ignited and the heterogeneous only steady states remain nearly constant as shown in Fig. 8. As explained later, this is a strong indication that the chemistry on the gauze surface is not affected by the gas phase composition and reactions are primarily the total oxidation of n-butane.

Similar to the 80 mesh gauze reactor, effects of flow rate and preheat variation were examined. Since the 40 mesh gauze allowed fuel leaner operation with reduced temperatures, the feed flow rate was now varied from 1 to 4 SLPM (instead of 2 to 4 SLPM). The results are shown in Fig. 6. Clearly, we see that, in general, the shape of the curves is similar to the 80 mesh gauze case. However, the operating window is now larger than before and for flow rates between 3 and 4 SLPM, the observed temperatures are up to 50°C lower.

The effect of preheat is shown in Fig. 7. In contrast to the 80 mesh gauze case, for preheats up to 250°C no significant changes are observed. Even for the highest preheat,

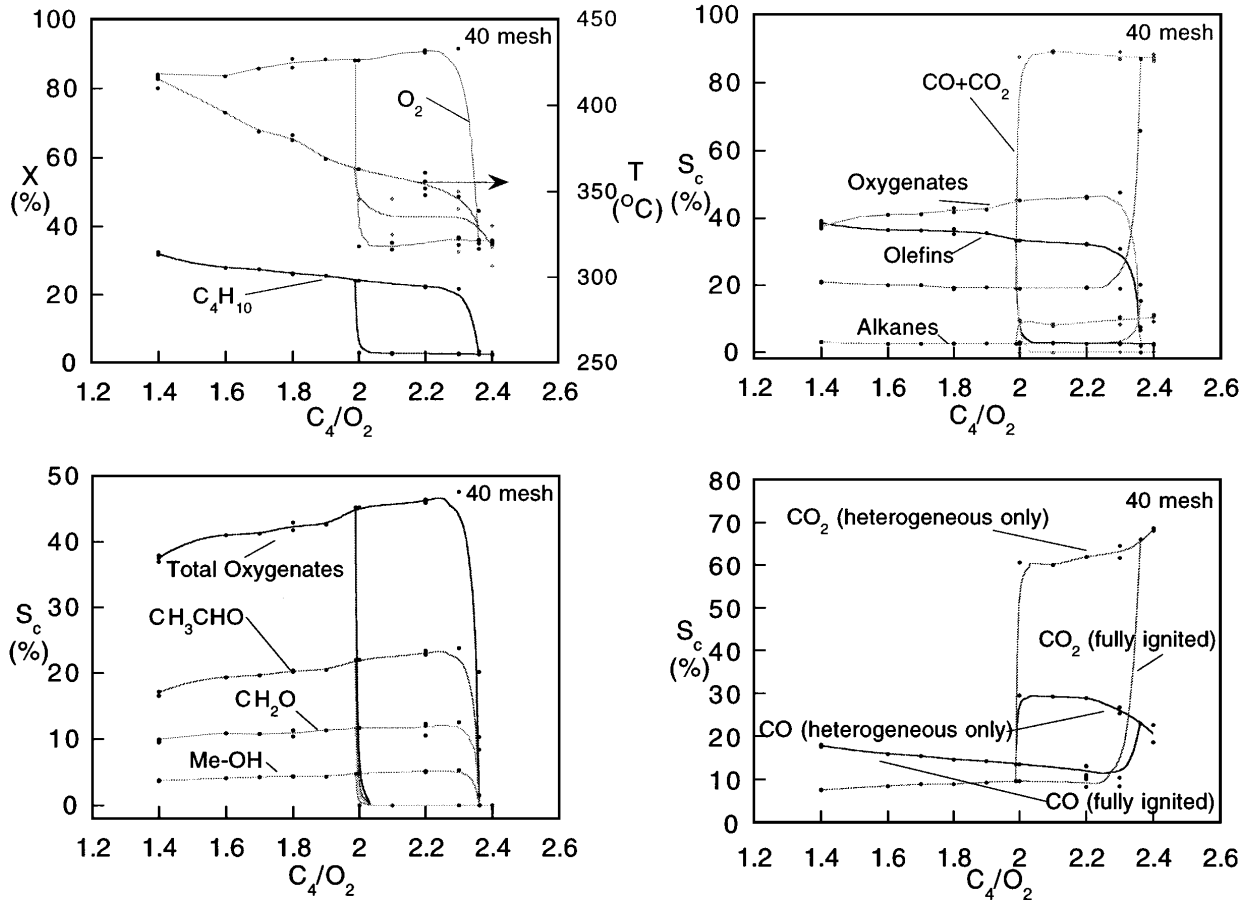

FIG. 5. Fuel and oxygen conversions, temperature, and product selectivities for a single 40-mesh Pt–10% Rh gauze reactor over a range of C_4/O_2 feed ratios. Flow rate is 2.5 SLPM; no N_2 diluent is present in the feed; no preheat. Both "fully ignited" and "heterogeneous only" steady states are shown.

all conversions and selectivities remain practically constant.

4. DISCUSSION

4.1. Overall Process

It was proposed (3, 4) that for oxygenates to form in this system, the gauze acted as a source of heat and radicals which mixed with the cold unreacted gases that bypass the gauze to promote homogeneous reactions. Surface reaction products are suggested to leave the gauze at ~800°C and rapidly mix with the bypassing cold stream. This process takes place in a few microseconds and results in rapid homogeneous reactions with simultaneous quenching to an exit gas temperature of 350 to 450°C. For large hydrocarbons (n-butane or larger) at temperatures lower than 900 K it was suggested that a chain branching mechanism takes place whose precursor is the ROO · radical (butylperoxy) (5, 11), which undergoes an intramolecular rearrangement to olefins and oxygenates. In this work, we found that the 40 mesh experiments exhibited two steady states, and in one of them only surface reaction occurs. We also found that of all products the total CO_2 yield is the only one that remains practically constant in both states (Fig. 8).

4.2. Steady State Multiplicity

These results strongly suggest a sequential operation of the gauze reactor:

Surface reactions. In the "heterogenous only" steady state, surface reactions are active and decoupled from any homogeneous reactions. Gases react exothermally on the gauze surface, forming primarily complete combustion products, CO_2 and H_2O, although some CO is also formed. We have no direct information on what radicals are produced on the catalytic surface, but the final product distribution suggests that most of them eventually decompose to combustion products. The only non-$(CO + CO_2)$ product species in the exit stream when homogeneous reactions are extinguished are 1-butene, isobutane, and neopentane and have a combined carbon atom selectivity of ~10%. The cold gases that bypass the gauze mix with the hot products which leave the catalytic surface, but no other chemistry is induced.

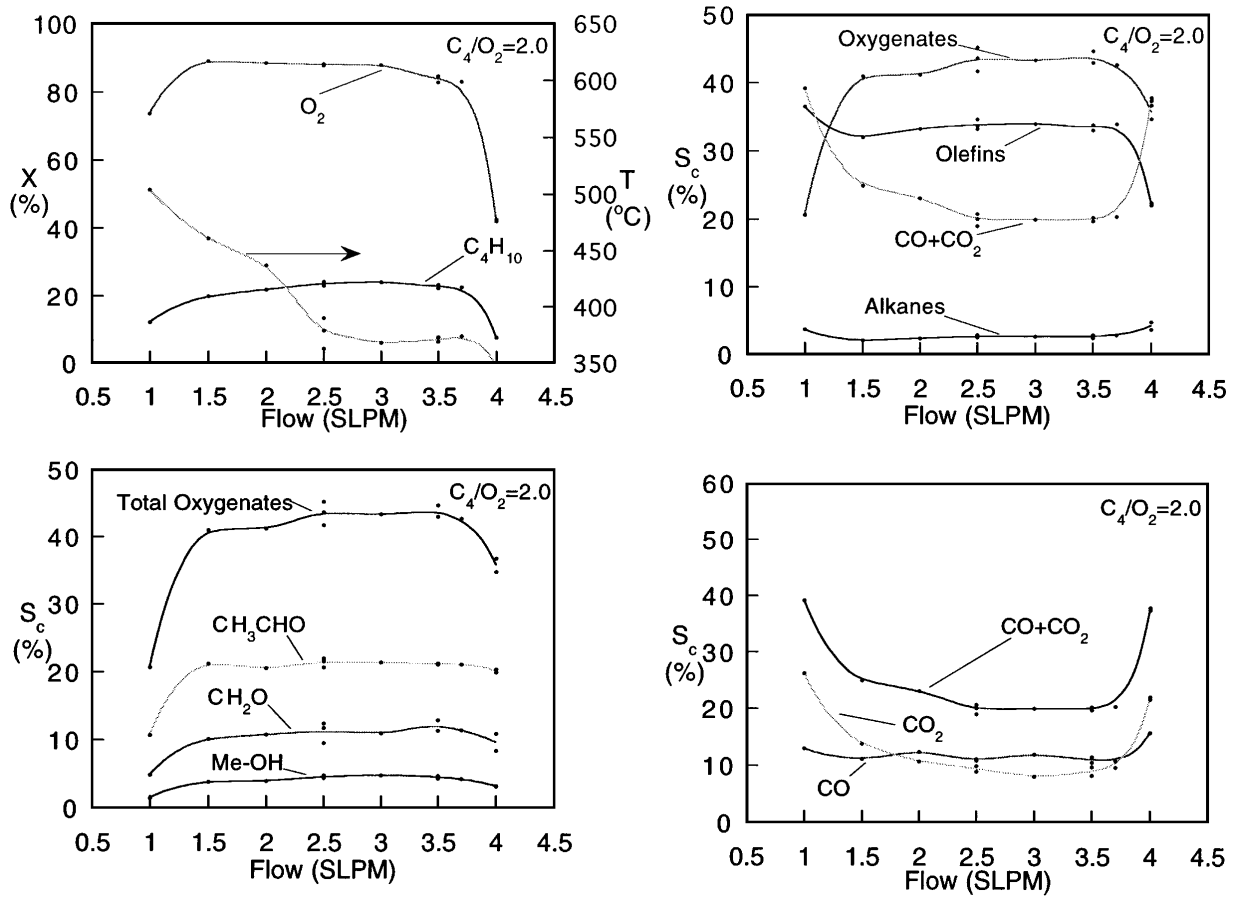

FIG. 6. Fuel and oxygen conversions, temperature, and product selectivities for a single 40-mesh Pt–10% Rh gauze reactor over a range of feed flow rates. C_4/O_2 feed ratio is 2.0; no N_2 diluent is present in the feed; no preheat. Only "fully ignited" steady states are shown.

Surface and homogeneous reactions. In the "fully ignited" state, however, the heat liberated from the exothermic catalytic combustion and the radicals produced on the surface initiate a sequence of homogeneous reactions which result in oxygenate and olefin production. Furthermore, the mixing of the hot and the cold gases produces rapid quenching of the effluent stream of temperatures of 350 to 450°C, and this prevents the decomposition of the oxygenates produced. The fact that total CO_2 yield is practically constant in both the "fully ignited" and in the "heterogeneous only" state shows that CO formation is primarily due to homogeneous hydrocarbon oxidation, whereas CO_2 production in the gas phase is minimal. This agrees with theoretical results reported by Warnatz that CO is the primary product of hydrocarbon oxidation and is converted to CO_2 in a subsequent slow secondary reaction (5). In contrast to CO_2, water does not follow similar reaction paths and therefore it would be wrong to derive similar conclusions by comparing H_2O yields between the two steady states.

An additional indication of this sequential operation is the fact that for increased flow rates the conversions and the product selectivities show the same behavior. In this case, the homogeneous reactions cannot be sustained but are "blown out" due to the high flow velocities, whereas heterogeneous reactions remain active, producing mostly CO_2.

4.3. Dilution and Chain Reactions

Another suggestive result was the effect of nitrogen dilution on the product distribution. Figure 2 shows that for nitrogen dilution larger than ~15% the oxygenate and olefin products drop dramatically. This suggests that increased partial pressure of inert gases in the feed stream effectively lowers the rates of homogeneous reactions which lead to oxygenate production. This is supported by modeling results as well (Section 4.5). From Fig. 2 it is seen that this change is smooth and does not appear to be discontinuous. The data points for dilutions from 0 to 15% show a gradual decrease in the oxygenates and olefins selectivity and simultaneously an increase in the $CO + CO_2$ selectivity. Thus, this effect is probably not the same as the "fully ignited" to "heterogeneous only" double steady state behavior mentioned earlier but rather an indication of a gradual effect of the inert gas in the homogeneous chain reaction sequence. Higher pressure experiments would verify this hypothesis

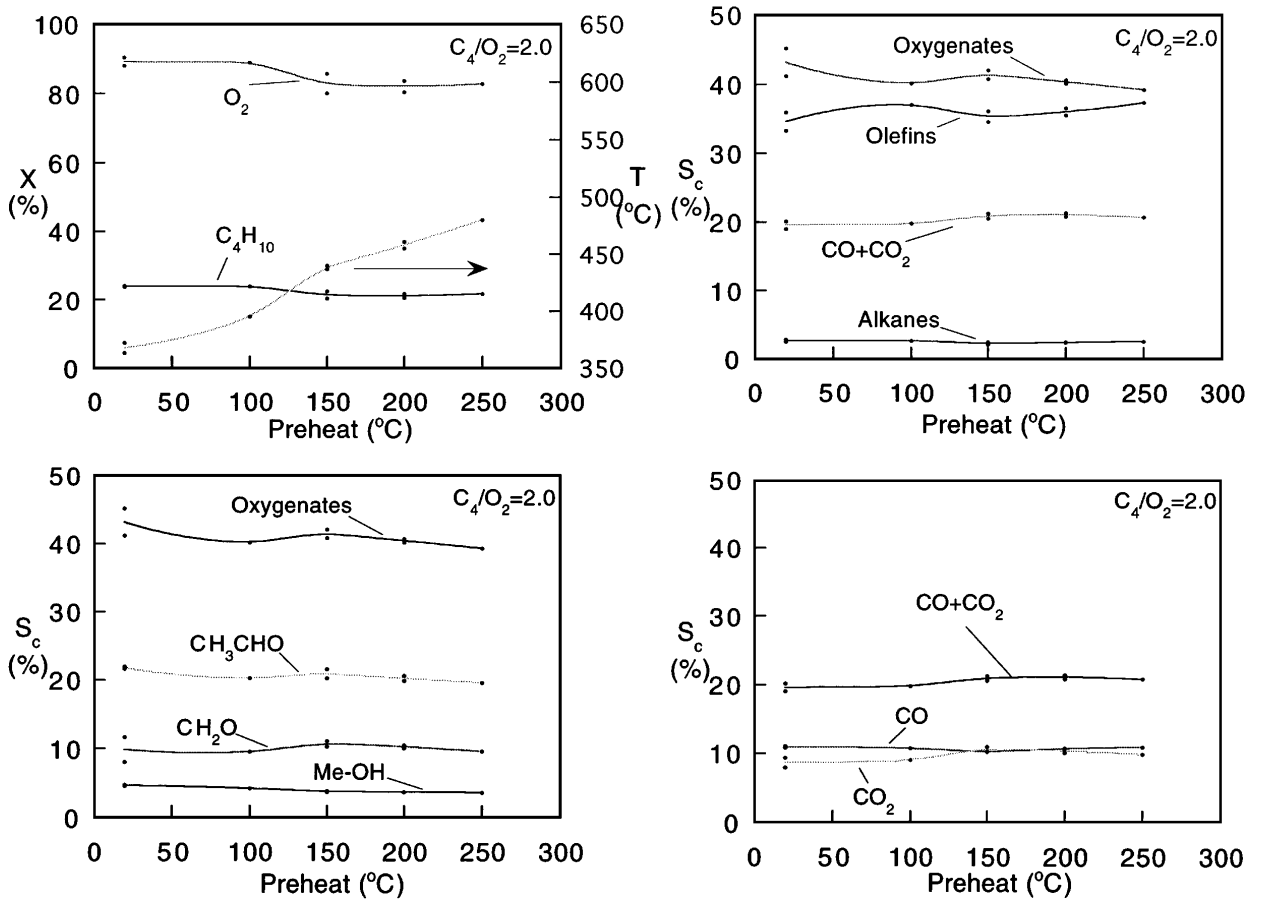

FIG. 7. Fuel and oxygen conversions, temperature, and product selectivities for a single 40-mesh Pt–10% Rh gauze reactor over a range of feed preheat temperatures. Flow rate is 2.5 SLPM; C_4/O_2 feed ratio is 2.0; no N_2 diluent is present in the feed. Only "fully ignited" steady states are shown.

because the role of homogeneous reactions should increase at high pressures.

4.4. Equilibrium

To examine how close the gauze reactor product distributions are to equilibrium, the HSC software package (10) was used to calculate the equilibrium compositions and typical results of these calculations are shown in Table 1. The thermodynamically stable products in the temperature range of 300 to 500°C were calculated to be primarily CH_4 and CO, followed by CO_2, C_2H_4, C_2H_6, and C_3H_6. Only trace amounts of oxygenate compounds are predicted at chemical equilibrium. In Table 1, equilibrium results are compared to typical experimental data for a n-C_4/O_2 feed ratio of 1.4 with no nitrogen dilution. The difference from the experiments is striking and shows how distinct the gauze reactor is in its operation because it is able to "freeze" intermediate products even in the case when they are not thermodynamically stable.

4.5. Simulation of Homogeneous Reactions

It is important to compare experimental results of gauze reactors with simulations using detailed chemistry. However, one should consider two facts: First, no heterogeneous detailed model for catalytic partial oxidation of n-butane on Pt/Rh yet exists in the literature. Thus, detailed n-butane modeling calculations must be done using homogeneous elementary mechanisms only. Second, existing homogeneous models with detailed chemistry involve hundreds of species and hundreds or thousands of reactions. For this reason, numerical solutions with reasonable computation times can be obtained only for simple reacting configurations alone (e.g., plug flow or batch reactors). Two-dimensional modeling attempts with complete detailed chemistry models involving complicated geometries and diffusion require ample effort and simplifying assumptions. We are extensively working in this direction.

We performed calculations assuming plug flow with a prespecified temperature profile with a mechanism developed by Warnatz and co-workers (12) which uses an elementary homogeneous reaction scheme involving 1777 irreversible reactions and 239 species. The computer program simulates an isothermal plug flow reactor with homogeneous chemistry only at variable residence times. In Table 1 we compare representative modeling results with typical results of the

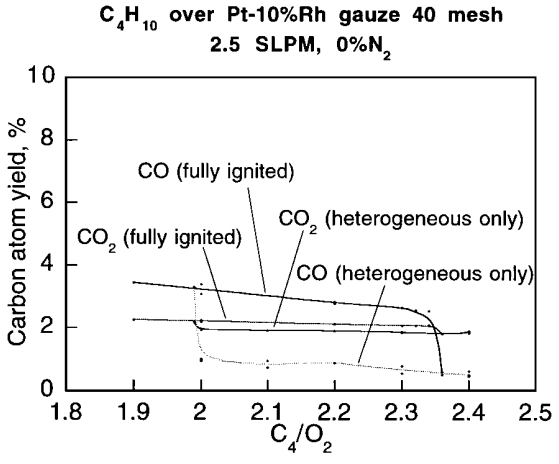

FIG. 8. CO and CO_2 carbon atom yields for a single 40-mesh Pt–10% Rh gauze reactor over a range of C_4/O_2 feed ratios. Flow rate is 2.5 SLPM; no N_2 diluent is present in the feed; no preheat. Both "fully ignited" and "heterogeneous only" steady states are shown.

40 mesh gauze reactor (2.5 SLPM). Both systems refer to a n-C_4/O_2 feed ratio of 1.4 with no nitrogen dilution.

Oxygenate formation. Homogeneous chemistry is believed to result in significant oxygenate formation and this is verified by the simulations. The experimentally observed oxygenate selectivities are higher than the calculated ones, but homogeneous numerical "experiments" correctly predict the experimental trends: Low temperature (680 K) isothermal runs with variable n-C_4/O_2 feed ratios predict that, as n-butane increases in the feed, oxygenate selectivity increases and begins at shorter residence times. Constant temperature runs with variable feed dilution predict that as N_2 increases in the feed, oxygenates become less and form

TABLE 1

Comparison between Gauze Reactor Experiments, Homogeneous Modeling Calculations and Equilibrium, of n-Butane Conversions and Main Product Selectivities

	Experiments, 690 K, Pt–10% Rh gauze	Model 690 K, 1.3 s	Equilibrium 690 K
Percentage C_4H_{10} conversion	31.8	38.1	100.0
Percentage selectivities (C atom basis)			
CH_4	1.42	0.71	59.81
C_2H_4	6.62	<0.01	0.97
C_3H_6	6.37	7.99	1.43
1&2-C_4H_8	25.47	13.22	0.48
CH_2O	9.71	6.52	<0.01
CH_3CHO	17.16	13.37	<0.01
CH_3OH	3.61	3.85	<0.01
CO	14.69	17.01	35.55
CO_2	6.22	3.07	0.08

Note. Fuel/oxygen ratio = 1.4.

at longer residence times. We will describe details of these simulations in a later paper.

Effect of seeding and various temperature profiles on residence times. The most significant discrepancy between the model predictions and the experiments are in the residence times where maximum oxygenates are formed. Whereas in the experiment we have contact times in the order of milliseconds, calculations predict maximum oxygenates at much longer residence times in the absence of a gauze. We believe that the importance of the catalytic wire is significant in this sense. Apart from the necessary heat to drive the reaction, the wires might provide radicals which ignite the chemistry much sooner than computationally predicted. Low (700 K) temperature seeding runs with various radicals such as O, H, OH, HO_2, p-C_4H_9, s-C_4H_9, p-C_4H_9O, s-C_4H_9O, p-C_4H_9OOH, s-C_4H_9OOH, reduced the time required for maximum oxygenate production down to ~100 ms, but this caused a slight decrease in oxygenate selectivity.

Higher constant temperature (1100 K) seeding runs reduced further this time. We also ran simulations with variable temperature profiles such as a step between ~1100 and ~700 K with and without seeding. In all such cases we tested, maximum total oxygenate selectivity was well below 10%. Of all simulations, the temperature profiles which led to significant oxygenate production were constant with low temperatures.

Necessity for 2D simulations. The product distribution in Table 1 indicates that a complete calculation should combine surface chemistry which results in CO_2, CO and radical formation (seeding) with homogeneous chemistry, species diffusion, and heat transfer. A simplified 2D representation of the reacting system, including the flow field, is essential since the feed experiences a very complex temperature and mixing history. Seeding and high temperatures near the gauze can ignite the system and yield the olefins observed. Lower temperatures further from the gauze can then yield the reported oxygenates. Such calculations are in progress.

5. CONCLUSIONS

Oxygenates and olefins are produced from n-butane partial oxidation with greater than 70% selectivity over a single layer of woven Pt–10% Rh gauze. Using two different mesh sizes, we found that the product yields can be improved when using the more open gauze. Furthermore, we observed multiple steady states in the operation of the gauze reactor with the more open mesh. Analysis and comparison of the product distribution of the two steady states revealed that the CO_2 is the only product whose yield remains practically the same in both cases. This suggests that the main catalytic reaction occurring on the gauze surface is probably the exothermic complete combustion of n-butane which supplies most of the heat necessary to initiate the

homogeneous reaction sequence that produces oxygenates and olefins.

In addition, experiments showed that there is significant effect of the nitrogen dilution on the product distribution. This is not due simply to temperature effects, since preheat experiments showed a different trend in the product distribution.

Homogeneous reaction modeling indicates that oxygenates are produced primarily from homogeneous reactions, although the experimental oxygenate selectivity is significantly higher than models predict.

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