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Oxygenates and Olefins from Alkanes in a Single-Gauze Reactor at Short Contact Times[1]

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Partial oxidation of linear C_1–C_5 alkanes in single-gauze reactors has been examined in the fuel-rich regime at contact times as low as 100 μs. We show that, whereas methane and ethane produce mostly CO and ethylene, respectively, propane, butane, and pentane give high selectivity to oxygenates and olefins. Partial oxidation of propane over a single gauze gives a total selectivity to olefins of nearly 60% with a 2/1 C_3H_6/C_2H_4 ratio and minimal oxygenates. Butane oxidation gives a significant amount of oxygenated products, mainly acetaldehyde and formaldehyde with a more open gauze, giving better selectivities. Pentane oxidation gives the highest oxygenate selectivities (up to 60%), the main products being acetaldehyde and propionaldehyde. We argue that this is a coupled heterogeneously initiated homogeneous reaction system, with total combustion primarily catalyzed by the Pt surface and the oxygenates and olefins formed subsequently by gas-phase reactions.

1. INTRODUCTION

A reactor consisting of a single layer of woven metal gauze is a novel catalytic system for alkane oxidation with several unique characteristics (1–3). Autothermal partial oxidation of hydrocarbons over single gauzes combines surface reactions with gas-phase chemistry under fast mixing and quenching conditions at very short contact times. This process forms mostly nonequilibrium products which are currently made by multiple-stage, energy-intensive processes. In this paper, we extend previous work on single-gauze reactors to a range of linear hydrocarbon feeds and examine its potential for production of chemicals.

Olefins such as ethylene and propylene are important chemicals, whose manufacture attracts the attention of many researchers. Typical production methods, which are still producing large pieces of literature, are steam cracking (16), catalytic cracking (17–19), and oxidative dehydrogenation (20–22). For many thermal methods (4) C_2H_4 and C_3H_6 production is simultaneous and reported carbon selectivity ratios range from 60/1 (C_2H_4/C_3H_6) to 1.5/1 (5), with a significant portion of the feed being converted to methane. Huff *et al.* have shown that selective production of ethylene can be achieved upon feeding ethane and oxygen in a Pt-coated monolith reactor (7). They also showed that using propane as a feed in the above reactor can give ~1/1 C_2H_4/C_3H_6 ratio (8), a significant improvement since propylene-rich product streams are particularly desirable. Recent results using Pt–Sn catalysts with H_2 addition in the feed give olefin selectivities higher than 85% (15). In all of these situations, less than 1% total selectivity to oxygenated products was observed.

Oxygenates such as low molecular weight aldehydes are widely used in industrial organic synthesis. A lot of research is generated on aldehyde production from alcohol oxidation (23) or acid reduction (24). Of great interest are methods on direct oxygenate production from alkane feeds (25, 26). Goetsch *et al.* (1, 2) showed that a mixture of *n*-butane and oxygen fed in a single-gauze reactor gave at least 40% selectivity of oxygenated products with contact times in the order of milliseconds.

2. EXPERIMENTAL

We fed C_1–C_5 linear hydrocarbons premixed with oxygen and nitrogen to single-gauze reactors and ran autothermally at short contact times, investigating conditions for potentially high selectivities to specific products. Gauzes were 99.9% pure Pt–10% Rh, with a wire diameter of 90 μm and either 40 or 80 mesh (wires per inch), corresponding to 640- or 320-μm wire spacing.

The reactor, catalysts, and procedure used in these experiments have been described previously (3). We used a syringe pump with 500-ml capacity and variable flow rates up to 420 ml/h to feed the liquid hydrocarbon through a coil pipe in a fluidized bed heater at a pressure of ~800 kPa (9). The gasified fuel was then expanded to reactor operating pressure. Before mixing with the oxygen and nitrogen, the hydrocarbon vapors passed through a superheater to eliminate condensation.

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3. RESULTS

3.1. *Methane and Ethane*

Methane and oxygen were fed over a 80-mesh gauze at a flow rate of 2.5 slpm and 20% nitrogen dilution. Typical results are shown in Figs. 1a and 1b. Over a range of CH_4/O_2 ratios, methane conversion varied between 21 and 15%. Despite the large gauze transparency, oxygen conversion was always above 90%. This is surprising since no oxygen is expected to be consumed in the gas phase under these operating conditions. This means that catalytic consumption rates of oxygen are very high. CO selectivity was relatively high, between 65 and 80%. However, total oxidation dominates H-atom consumption, resulting in H_2 selectivities $<10\%$.

Similarly, a mixture of ethane and oxygen was fed over a 80-mesh gauze and the results are shown in Figs. 1c and 1d. Between C_2H_6/O_2 ratios of 1.7 and 2.3, the ethane conversion changed from 85 to 55%, while oxygen was almost completely converted. Ethylene selectivity was between 60 and 65%, and other products included CO, CO_2, and CH_4. These results are comparable to those obtained by Huff *et al.* (7) over Pt-coated monoliths at a residence time of about 5 ms.

3.2. *Propane*

The possibility of selectively producing propylene from propane was examined. As mentioned earlier (1, 2) and seen in this work, oxygenates are a small by-product in this process. Experiments were done using both 80- and 40-mesh gauzes, at a total flow rate of 2.5 slpm and 20% nitrogen dilution, varying the fuel-to-oxygen ratio. Results are shown in Fig. 2.

80-mesh gauze. Three operating regimes can be identified: with C_3/O_2 varying from 1 to 1.7, propane conversion exhibited highest values close to 90% while oxygen was completely converted. The dominant olefin was ethylene and CO selectivity was higher than that of CO_2. For C_3/O_2 varying from 1.7 to 2.8, the dominant olefin changed from ethylene to propylene. Fuel conversion dropped from 55 to 20% but oxygen was still completely converted. At a ratio of 2.8, the propylene-to-ethylene selectivity ratio was 2/1 and propylene selectivity was 37%. Finally, for $C_3/O_2 > 2.8$, oxygen breakthrough was observed and CO_2 selectivity increased dramatically. The reactor was practically extinguished, mostly producing combustion products.

40-mesh gauze. Results were similar to those of the 80-mesh gauze, but in this case, oxygen conversion was always

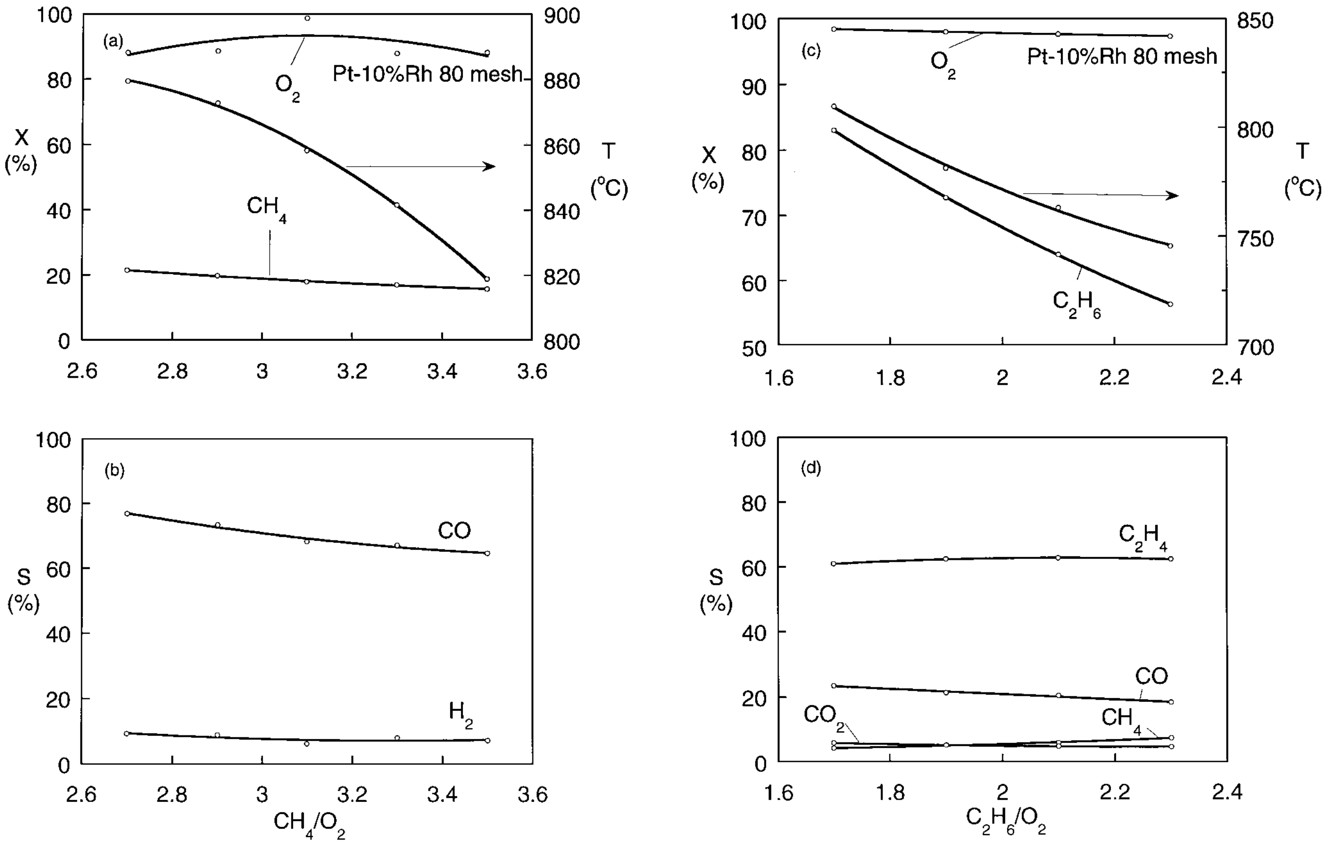

FIG. 1. Fuel and oxygen conversions, temperatures, and product selectivities for a single 80-mesh Pt–10%Rh gauze reactor over a range of fuel/oxygen feed ratios. Experimental results for the methane feed are shown in Figs. 1a and 1b, and for the ethane feed are shown in Figs. 1c and 1d.

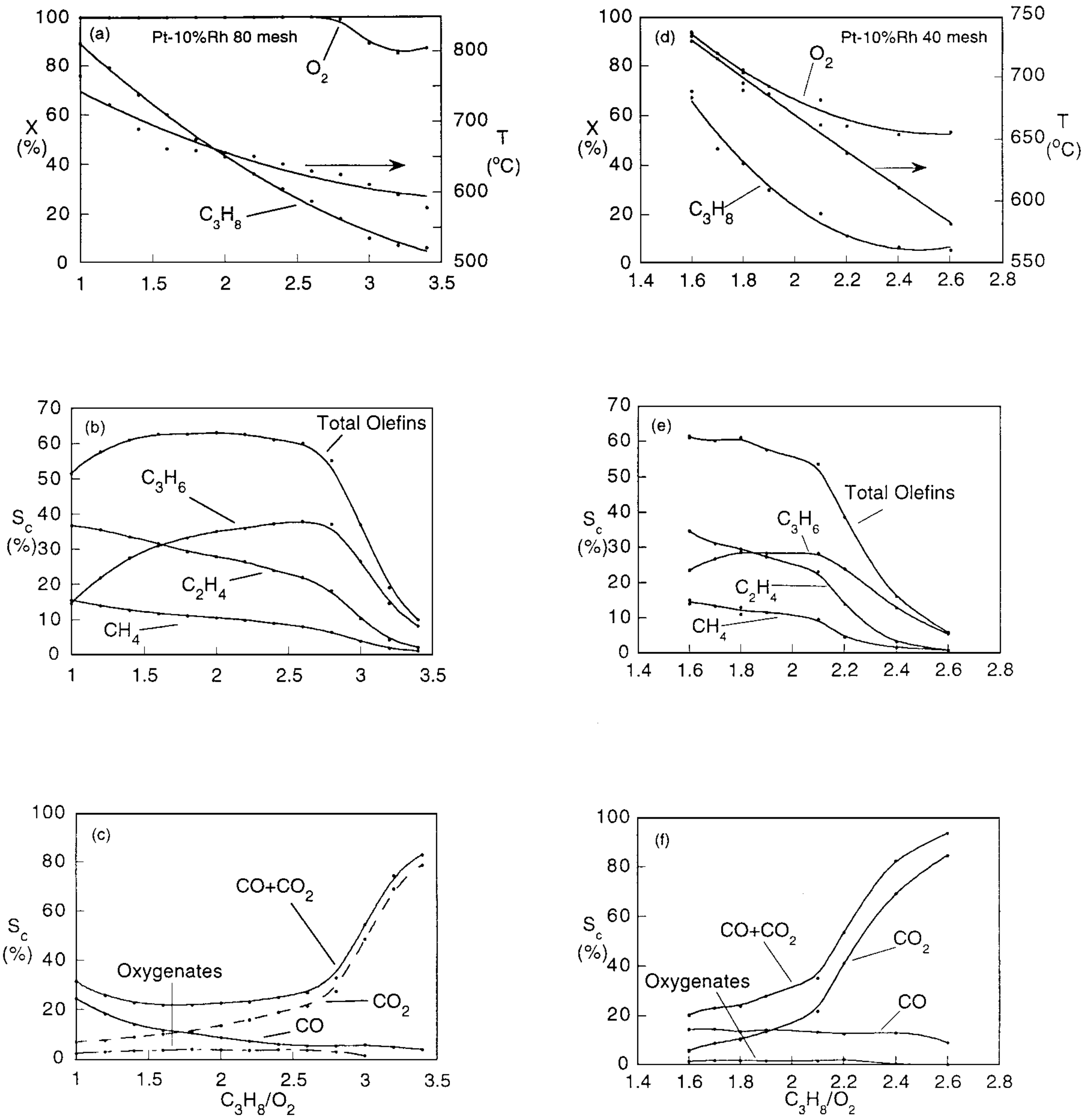

FIG. 2. Fuel and oxygen conversions, temperature, and product selectivities for *n*-propane feed over a single Pt–10% Rh gauze reactor for a range of fuel/oxygen feed ratios. The results for the 80-mesh gauze are shown in Figs. 2a–2c, and for 40-mesh gauze the results are shown in Figs. 2d–2f.

incomplete. Propylene vs ethylene selectivity ratios were higher on the 80-mesh gauze.

3.3. *n-Butane*

n-Butane was the lightest fuel to yield significant oxygenated products (1, 2). It was proposed and later confirmed (3) that oxygenates are produced by gas-phase chemistry only. The results using *n*-butane feed have been published earlier and we refer the reader to the original publication for more details (3). Here, we mention only the most important features.

Over an 80-mesh gauze and for an *n*-C_4/O_2 ratio between 2.3 and 3.0, the main products were oxygenates, with a selectivity of ~40%. Olefin selectivity was around 30% and the combined $CO + CO_2$ selectivity did not exceed 30%. For a ratio above 3.0, considerable reduction of conversions and olefin and oxygenate selectivity occurred, with *n*-butane and oxygen conversions dropping to 5 and 60%, respectively. This change appears to be reversible with *n*-C_4/O_2 feed variation. Negligible oxygenates and olefins were produced, main products being CO and CO_2.

A 40-mesh gauze gave higher oxygenate selectivities and butane conversions with leaner operation. For a small range of *n*-C_4/O_2 feed ratios, two stable steady states were observed and reproduced on several gauzes. In the first steady state, oxygen and fuel conversions were high, whereas in the

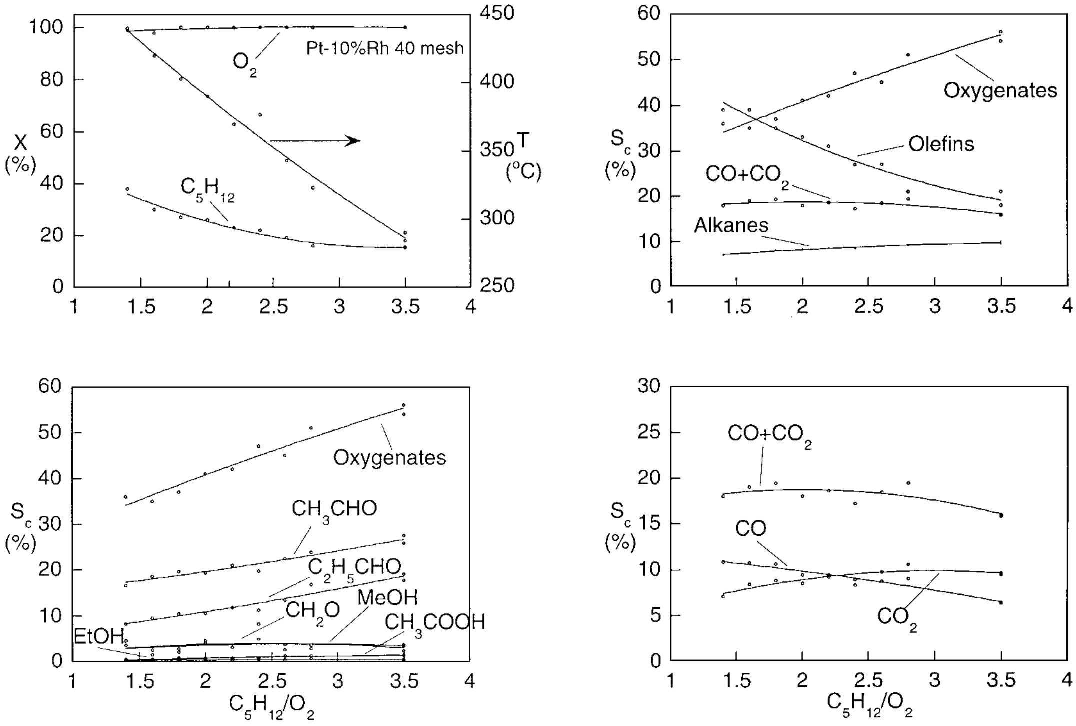

FIG. 3. Fuel and oxygen conversions, temperature, and product selectivities for *n*-pentane feed over a single 40-mesh Pt–10% Rh gauze reactor for a range of fuel/oxygen feed ratios. Reactor operating pressure is 120 kPa.

second they were much lower. Oxygenates were formed in one steady state only, and in the other CO and CO_2 were the main products. An important observation was that CO_2 yields remained constant in both steady states (3).

3.4. n-Pentane

Since *n*-butane oxidation gave higher selectivities to oxygenated products using a 40-mesh gauze, we ran pentane experiments with this mesh size only. Typical results are shown in Fig. 3. Over the entire $n\text{-}C_5/O_2$ range, oxygen conversion was complete. *n*-Pentane conversion varied from 40% in the fuel-lean side to 20% in the fuel-rich side. Exit gas temperatures were between 440 and 280°C. Olefins were the dominant products in the fuel-lean regime. For $n\text{-}C_5/O_2 > 1.7$, oxygenate selectivity was higher than that of olefins, varying from 35 to 58%. The maximum selectivity was about 10% higher than that seen with *n*-butane. Acetaldehyde was still the major oxygenated product with 27% selectivity and propionaldehyde was next with 18% selectivity. The selectivity ratio of these products varied from 1/1 to 3/2 from the fuel-lean to richer side. Other minor oxygenated products were also observed, including formaldehyde, methanol, acetic acid, acrolein, and ethanol, with all selectivities below 5%. $CO + CO_2$ selectivity never exceeded 20%.

Higher pressures. We ran pentane oxidation experiments at pressures up to 195 kPa. Flow rate, preheat, nitrogen dilution, and $n\text{-}C_5/O_2$ were kept constant, and the pressure varied from 120 to 195 kPa. Results are shown in Fig. 4. Elevated pressures increase fuel conversion significantly as expected. The conversion almost doubled upon increasing the pressure from 120 to 195 kPa. Oxygenate selectivity decreased and olefins were the major products at higher pressures. In these experiments, two main regimes were identified: for pressures below 160 kPa, oxygenate and total CO_x selectivity dropped and olefin selectivity increased upon increasing the pressure. For pressure above 160 kPa, conversions and selectivities did not vary significantly. Exit gas temperatures increased from 480 to 540°C.

We also ran experiments at a constant pressure of 191 kPa, varying the $n\text{-}C_5/O_2$ ratio, and the results are plotted in Fig. 5. A much higher conversion was obtained, exceeding 60%. The temperature was ~100°C higher than that in low-pressure experiments. Up to an $n\text{-}C_5/O_2$ ratio of 2.8, olefins were the major products. Above this ratio, oxygenate selectivity was higher. Maximum oxygenate selectivity approached 50%, with acetaldehyde and propionaldehyde being the most important products.

3.5. Gauze Activation

Activation of catalyst gauzes with time is very important (10, 11). Fresh gauze has a smooth surface and, after several hours of operation, the surface restructures dramatically (1, 10). The morphology of a used gauze indicates that the activation mechanism is similar to that of ammonia

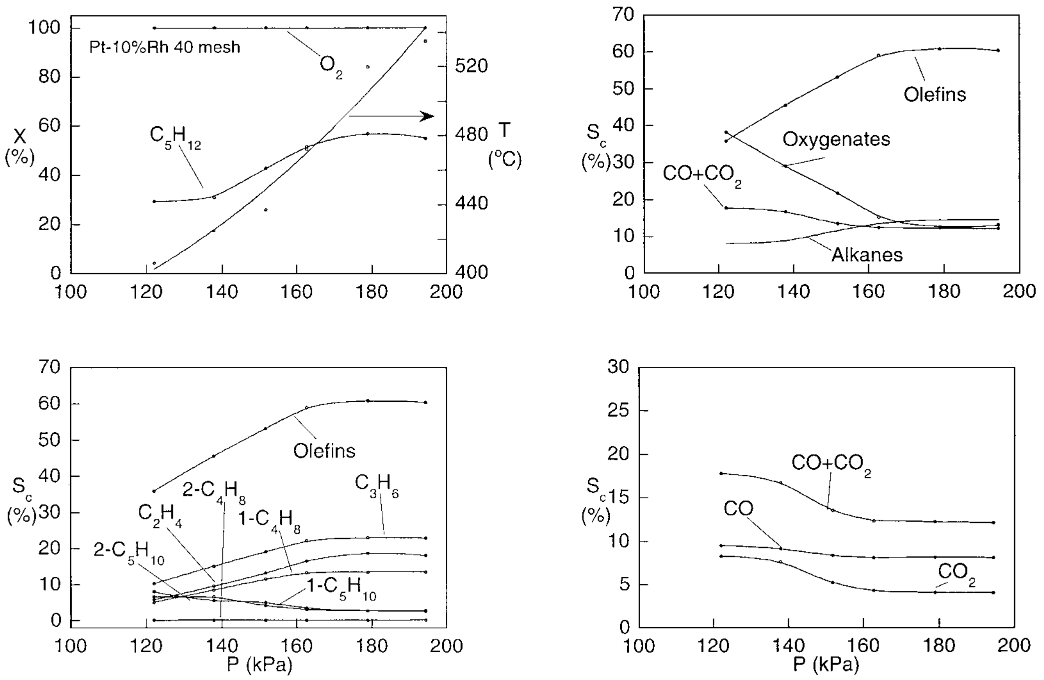

FIG. 4. Fuel and oxygen conversions, temperature, and product selectivities for *n*-pentane feed over a single 40-mesh Pt–10% Rh gauze reactor for a range of reactor operating pressures.

oxidation and HCN production (10). Conversions and selectivities improve significantly during the activation period before reaching a steady state. After reaching steady state, the gauze surface shows no further restructuring, as observed by SEM. The activation period can vary from a few hours to several days, depending on the fuel used and the reaction temperature. Attention was paid to avoid gauze deterioration. Repeated high-temperature experiments with

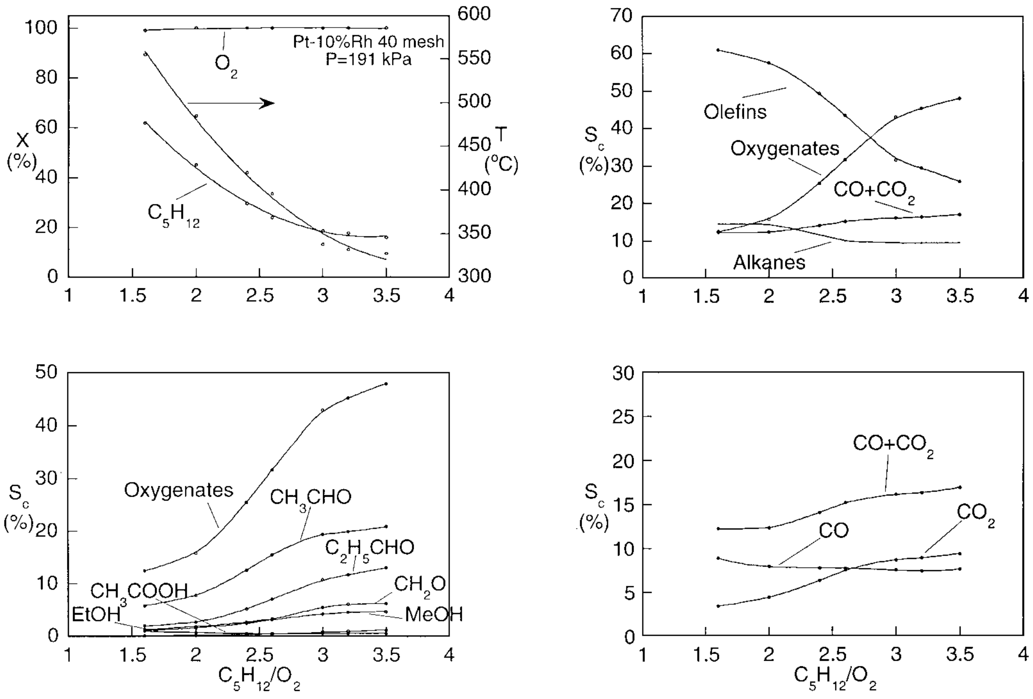

FIG. 5. Fuel and oxygen conversions, temperature, and product selectivities for *n*-pentane feed over a single 40-mesh Pt–10% Rh gauze reactor for a range of fuel/oxygen feed ratios. The reactor operating pressure is 195 kPa.

extreme composition variations sometimes resulted in gauze disintegration, especially during partial oxidation of C_1–C_3, where the catalyst temperatures can be very high. All the results reported in this work are from experiments where gauze deterioration was not an issue.

With methane feed, the gauze activated in only a few hours and exhibited the highest exit gas temperatures. Gauze activation with higher alkanes took much longer because temperatures were lower. Before being able to obtain consistent and reproducible data with *n*-pentane, several days were required. With all fuel feeds, we observed lower fuel and oxygen conversions and higher CO and CO_2 selectivities during initial runs.

For a more systematic study of gauze activation, experiments were done with propane using a 40-mesh gauze and the results are shown in Fig. 6. The C_3/O_2 ratio was kept constant at 1.6 and nitrogen dilution was 20%. In the first 5 h, the fuel conversion was below 10%, oxygen conversion was below 30%, and $CO + CO_2$ selectivity was above 80%. It is very interesting that selectivities to all products reached a steady value after about 8–9 h of operation, but it took at least 3–4 more h for the conversions to stabilize. This was also observed with other fuels. For example, both butane and pentane oxidation gave a steady selectivity to oxygenates much before the fuel and oxygen conversions became stable.

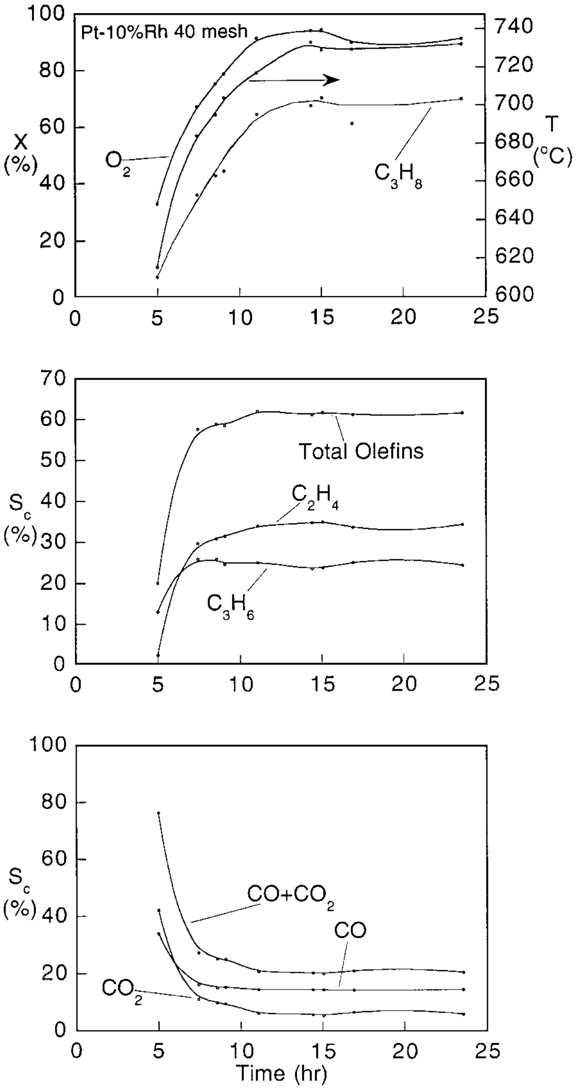

FIG. 6. Fuel and oxygen conversions, temperature, and product selectivities for *n*-propane feed over a single 40-mesh Pt–10% Rh gauze reactor during activation. The fuel/oxygen feed ratio is 1.6.

4. DISCUSSION

4.1. *Oxygenate and Olefin Formation*

CH_4 yields mostly CO and H_2O and C_2–C_5 linear alkanes give 60–80% selectivities to olefins and oxygenates. However, oxygenates are produced in significant quantities only when there are at least four carbon atoms in the backbone of the hydrocarbon feed. C_2H_6 and C_3H_8 give mostly olefins.

Methane and ethane. Results for methane oxidation show high CO selectivity (~80%) and very low H_2 selectivity (~10%). For production of syngas, Rh-coated monoliths give much higher yields (6). Results for ethane oxidation show C_2H_4 selectivities between 60 and 65%, comparable to those obtained on Pt-coated monoliths. Since residence times in gauze reactors are at least 50 times shorter than those over monoliths, these results show that Pt-catalyzed oxidative dehydrogenation of ethane is an extremely fast process and only a minimum amount of the noble metal is required for the reaction to go to completion.

Propylene from propane. Using propane as the fuel, we observe significant amounts of propylene. In this reaction ethylene is an important by-product. Recent results of propane oxidation over monoliths have shown that the C_3H_6/C_2H_4 ratio can be as high as 1/1 (8). We find that this product ratio can be further improved and can be as high as 2/1 using 80-mesh gauze.

Oxygenates from n-C_4 and n-C_5. With butane as the feed, we observe significant amounts of oxygenated products, primarily acetaldehyde and formaldehyde. A single gauze is the only configuration to give significant selectivities to these nonequilibrium products during fast autothermal operation. A more open gauze gives higher selectivities to oxygenates. The gas and surface reactions can be decoupled over the more open gauze, resulting in multiple steady states (3).

With pentane feed, a 100°C preheat was applied in all runs to avoid condensation. Maximum oxygenate selectivity approached 60%. Only the 40-mesh gauze was used since the more open gauze is favorable for oxygenate production. The main oxygenated products from pentane are C_2 and C_3 aldehydes rather than C_1 and C_2 aldehydes from butane. Oxygen conversion is complete throughout the

n-C_5/O_2 feed range, in contrast to butane experiments. This makes pentane more attractive since the presence of oxygen in the exit stream makes product handling dangerous.

In n-C_4 experiments, the oxygenate selectivities rapidly dropped above C/O ~ 4.7. With n-C_5, we ran up to C/O ~ 8.7 without seeing any decrease in oxygenates. This can probably be attributed to the increased gas-phase reactivity of pentane compared to that of butane. In addition, n-C_5 runs much colder than n-C_4 and lower temperatures promote higher oxygenates production because their decomposition is minimized. The exit gas temperature is ~50°C lower than that in n-C_4 experiments at the rich limit.

Pressure effects. In Fig. 4, it is seen that higher pressure has a significant effect only up to 160 kPa and above this there are not many changes in the chemistry. CO production may be a key factor in this situation in that CO is the only major species whose selectivity remains constant between 120 and 195 kPa. This means that its total yield is rising, thus consuming oxygen atoms which could otherwise go toward oxygenate production.

Varying the n-C_5/O_2 ratio at higher pressure (191 kPa) results in significantly higher fuel conversion, especially in the fuel leaner regime. The trade-off is a decrease in oxygenate selectivity, presumably because of the higher temperatures observed.

In general, the fact that pressure strongly influences experimental results confirms the importance of homogeneous chemistry. However, it appears that we cannot easily increase fuel conversion without decreasing oxygenate selectivity in an insulated gauze reactor. For a commercial process heat removal from the system should probably be implemented to avoid production of other chemicals such as olefins and CO_x at the expense of oxygenates.

Comparison of fuels. In Fig. 7, conversions and major product selectivities of C_3H_8, C_4H_{10}, and C_5H_{12} are compared, for experiments with a 40-mesh gauze.

It is seen that butane and pentane exhibit similar behavior in that conversions and selectivities of both fuels have almost identical slopes. The pentane conversion is higher than butane by 5–10% for C/O between 3.5 and 4.5. As a consequence, the corresponding temperatures are about 50°C higher for n-C_5, and this results in lower oxygenates and higher olefin selectivities than with n-C_4. Butane oxygenate production maximizes at C/O ~ 4.5 and then the homogeneous chemistry extinguishes. Pentane, however, continues without gas-phase chemistry extinction. Conversions of C_4H_{10} and C_5H_{12} show that the two fuels behave in the same manner with respect to conversions and production of olefins and oxygenates. This was also confirmed by results shown in Fig. 9, where both fuels show experimental behavior with $\%N_2$ feed variation which was theoretically predicted by the same homogeneous chemistry mechanism.

In contrast, propane behaves much differently in that experimental conversion and selectivities to oxygenates and olefins have slopes and values which are quite different than those of butane or pentane.

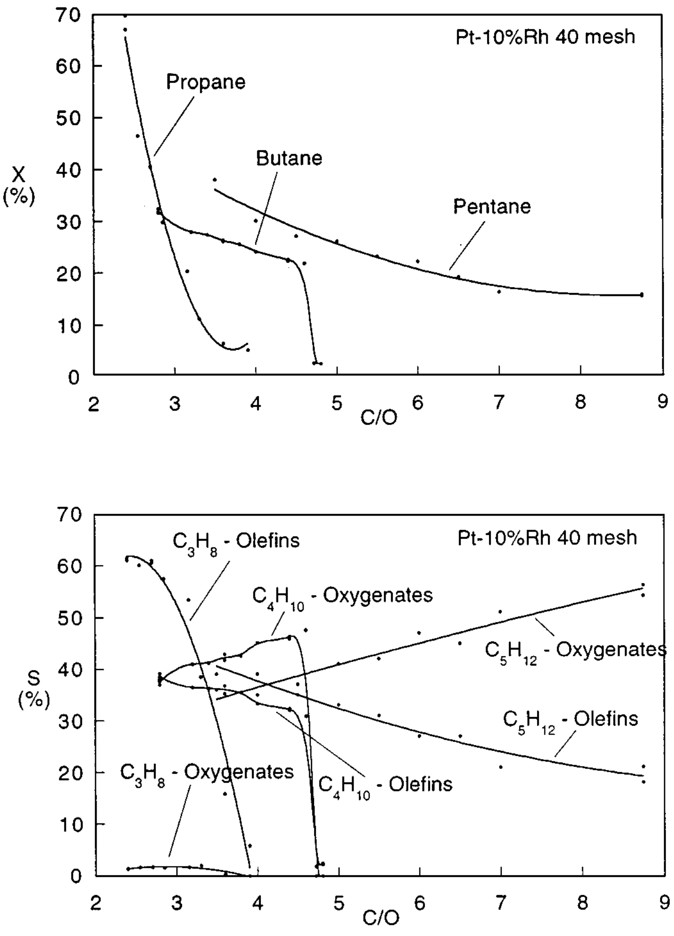

FIG. 7. Fuel conversions and oxygenate and olefin selectivities vs C/O feed ratio, for n-propane, n-butane, and n-pentane fuel feeds. The reactor is a 40-mesh single Pt–10% Rh gauze.

A reaction path analysis using gas-phase chemistry (Fig. 8) shows that the intramolecular rearrangement of peroxy radicals is the primary mechanism for oxygenates production for butane and presumably for pentane. The rates of similar reactions for propane were much lower, resulting in minimal oxygenates production.

4.2. *Modeling of Propane Oxidation*

The selective production of propylene rather than ethylene from propane feed is of economic importance. The major problem encountered in most existing processes is C–C cracking, which leads to ethylene and CH_4 (5, 8, 12).

It was found that the optimum selectivity ratio of C_3/C_2 olefins can be attained over the 80-mesh gauze. At a C_3/O_2 ratio ~2.8 and 20% nitrogen dilution, oxygen conversion was complete, the fuel conversion was 20%, C_3H_6 selectivity was 37%, and the C_2H_4 selectivity was 18% at an exit gas temperature of 630°C (Fig. 2). Selectivity to methane was 6%.

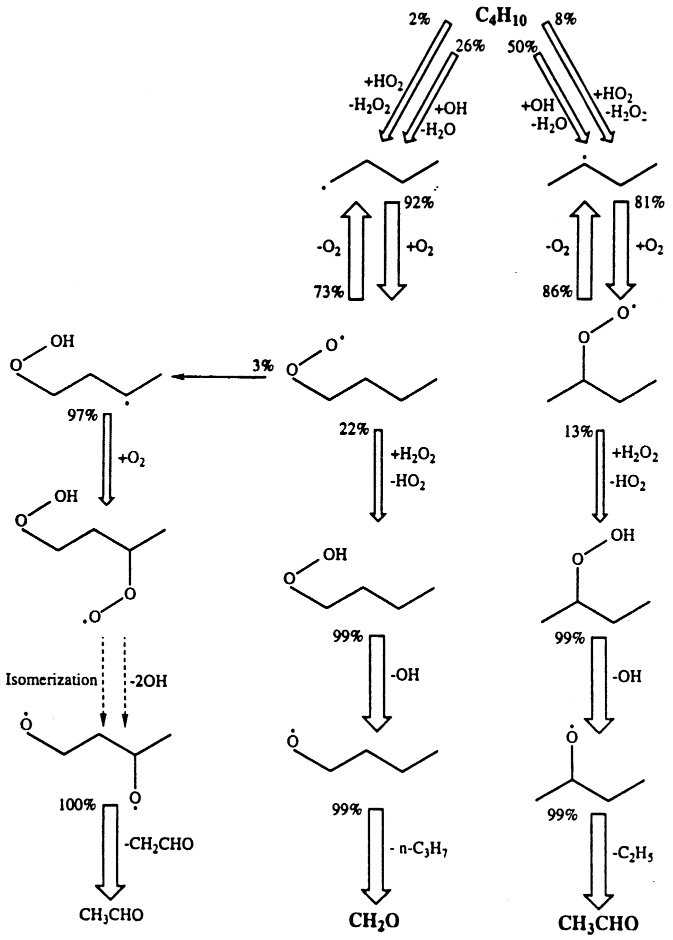

FIG. 8. Reaction path analysis for the homogeneous production of oxygenates from *n*-butane.

Equilibrium. At a C_3/O_2 feed ratio of 2.8 and 20% nitrogen dilution, we calculated the equilibrium composition at 630°C. As shown in Table 1, we found that at equilibrium both oxygen and propane conversions are complete, while C_3H_6 and C_2H_4 selectivities are only 6 and 12%, respectively. Equilibrium favors methane and CO formation, giving 56% CH_4 selectivity and 24% CO selectivity. Thus, we conclude that the experimental products are far from equilibrium and contain greater amounts of olefins than those predicted by thermodynamics.

Modeling. Single-gauze systems require complicated models to accurately predict and elucidate all the phenomena that take place during reactor operation. A rigorous modeling approach would involve three-dimensional (3-D) simulations (rather than two-dimensional (2-D) where additional assumptions should apply) of flow past woven Pt/Rh wires, involving detailed catalytic and homogeneous chemistry. An investigation of potential chemical interactions between the surface and gas phase is important. Sharp temperature gradients and mixing after the wires can drastically affect final product distribution. However, several issues delay the advancement of such modeling efforts: Detailed surface mechanisms for hydrocarbon oxidation on Pt and Rh are still under development. Current research efforts focus on CH_4 surface reactions. Single-gauze systems have economic potential for C_3 and higher oxidation systems. Until surface reaction mechanisms for these higher hydrocarbons are established, any detailed modeling attempts will be subject to skepticism. Gas-phase reaction mechanisms are also under development, even though current models can adequately simulate reactions of heavier hydrocarbons. Finally, even if reliable mechanisms existed for both surface and gas chemistry, the computational requirements for a 3-D detailed calculation are tremendous. We are extensively working in this direction and have recently performed 2-D simulations of methane partial oxidation in Pt- and Rh-coated monoliths with surface and gas-phase chemistry (27) and 2-D simulations of methane partial oxidation over Pt gauzes with surface chemistry only (28).

To obtain a measure of how well existing chemistry models agree with our experimental results, we performed simple zero-dimensional (0-D) calculations, assuming only homogeneous reactions and plug flow at a specified temperature profile, using a detailed homogeneous chemistry mechanism developed by Warnatz and co-workers (14, 29, 30, 31). The temperature profiles used were based on 2-D calculations which simulated the flow of cold gas over hot wires (no chemistry). This mechanism incorporates ~240 species including various aliphatic and aromatic compounds and ~2000 chemical reactions. Computer experiments were performed at a C_3/O_2 ratio of 2.8, 20% nitrogen dilution, and a final temperature of 900 K, using the following temperature profiles: (1) Constant temperature of 900 K; (2) initial temperature of 1200 K and a step change

TABLE 1

Comparison between Gauze Reactor Experiments, Homogeneous Modeling Calculations, and Equilibrium, of Propane Conversions and Main Product Selectivities for a C_3/O_2 Feed Ratio of 2.8 (Modeling Calculations Included Heterogeneous CO_2 Production Prior to Gas-Phase Chemistry)

	Fuel/Oxygen Ratio = 2.8		
	Experiments, 900 K Pt–10% Rh gauze	Model 900 K, 34.5 ms	Equilibrium 900 K
% C_3H_8 conversion	18.0	24.7	99.9
% O_2 conversion	98.0	99.9	100.0
% Selectivities (C atom basis)			
CH_4	6	3.9	56.2
C_2H_4	18	18.3	12
C_3H_6	37	36.6	6
CO	5	1.1	23.8
CO_2	28	19.8	<0.01

to 900 K after 10 μs; (3) initial temperature of 1200 K and a step change to 900 K after 100 μs. We found only a minor influence of the initial temperature profile. In all three cases, the species concentration profiles were calculated as a function of reaction time. The propylene and ethylene selectivities were almost identical to the experimental values, as was the calculated oxygen conversion and CO selectivity. An important difference was that the model predicted higher fuel conversion than that seen in the experiment. The selectivity to CO_2 was also different between calculations and experiments, with simulations predicting very small amounts. As reported earlier (3) this is expected since CO_2 is believed to be formed primarily on the catalyst surface.

Homogeneous modeling with heterogeneous combustion. To test this hypothesis, we ran simulations where we mimicked the catalytic chemistry, assuming that initially a fraction of the C_3H_8 and O_2 instantly reacts on the surface to produce CO_2 and H_2O. The total amount of CO_2 produced was taken to be equal to the experimental value. Then, the resulting mixture was allowed to react homogeneously at 900 K up to a residence time where the C_3H_6/C_2H_4 ratio was equal to 2. This combined heterogeneous–homogeneous calculation gives a much better agreement with the experimental results than the purely homogeneous one (Table 1). The only relatively large difference with the experiment is the residence time. In the experiment, contact times are of the order of 1 ms, while simulations predict a reaction time of around 35 ms. However, this discrepancy is not as big as that noticed previously with *n*-butane calculations (3). We suggest that certain radicals are produced catalytically and speed up the homogeneous ignition. This suggestion was reasonably validated when we seeded radicals like O, OH, H, and n-C_3H_7 and calculated residence times of 19 ms. However, this caused a slight decrease in C_3H_6 and C_2H_4 selectivities.

Overall, the following mechanism is proposed: The feed enters the reactor and part of it reacts catalytically on the gauze surface to produce primarily total oxidation products (CO_2 and H_2O), releasing a significant amount of heat. The remaining part of the feed reacts homogeneously at these high reaction temperatures to yield the final products. A similar mechanism was suggested for the production of olefins and oxygenates from the C_4 feed (3).

4.3. *Effect of Nitrogen Dilution*

The effect of N_2 dilution on oxygenate production from *n*-butane is shown in Fig. 9a. We recorded a small decrease in oxygenate selectivity for dilutions less than 15%. For values higher than 15%, a steady but gradual decrease in the oxygenate selectivity was seen.

We speculated earlier that this should be an effect of the homogeneous chemistry (3). We performed computer simulations with the same model as before, using *n*-butane fuel feed (calculations with *n*-pentane were not possible because the mechanism does not include n-C_5H_{12}). When oxygenate selectivity vs N_2 dilution was calculated, three types of behavior were recorded: (1) monotonic decrease of S_{OX} with increasingly negative slope; (2) increase of S_{OX} toward a maximum and then decrease; and (3) monotonic increase of S_{OX}.

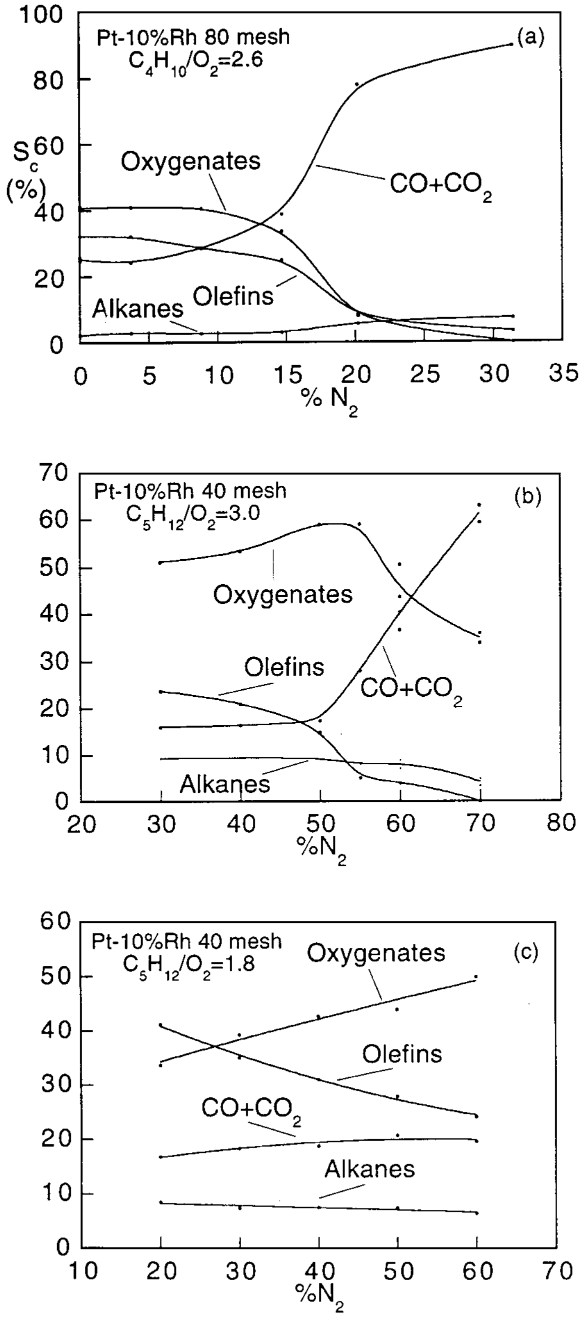

FIG. 9. Product selectivities vs feed N_2 dilution for *n*-butane and *n*-pentane. Figure 9a shows results for *n*-butane partial oxidation over a single 80-mesh Pt–10%Rh gauze and Figs. 9b and 9c show results for *n*-pentane partial oxidation over a single 40-mesh Pt–10%Rh gauze reactor, for two different fuel/oxygen feed ratios.

The predicted behavior (1) was experimentally observed in *n*-butane oxidation and is shown in Fig. 9a. Assuming that the chemistry-producing oxygenates is similar for all higher hydrocarbons, it should also be possible to observe behaviors like (2) and (3).

To verify this, experiments were performed with *n*-C_5 fuel with varying dilutions. The results are shown in Figs. 9b and 9c, and it is seen that the experimental trends do follow those predicted in the simulations. This suggests that *n*-C_5 oxidation has similar chemistry for oxygenate formation as that of *n*-C_4 and that N_2 dilution can be used as an important optimization parameter to maximize oxygenate selectivities.

5. CONCLUSIONS

A single Pt–10% Rh gauze reactor can be used for rapid production of chemicals such as olefins and oxygenates. Experiments and modeling from this and previous work suggest that a gauze reactor combines surface and gas-phase chemistry by oxidizing a part of the fuel on the catalyst surface to produce primarily CO_2 and release a lot of heat. This energy can be transferred to the remaining colder portion of the feed to ignite a homogeneous reaction sequence, which subsequently produces olefins and oxygenates. Simultaneously, fast quenching due to mixing lowers the exit temperature and prevents the decomposition of oxygenates.

Our reactor could process ∼6.5 kg/day of pentane and produce oxygenated species with carbon yields up to ∼1 kg/day, from a 15-mm gauze. If that was replaced with a 1-m diameter gauze reactor, the production would rise up to ∼4 t/day. It is obvious that, after optimization and recycling, a plant using this technology could produce large amounts of oxygenates and olefins with one relatively cheap reactor, avoiding expensive multistage processes and exotic catalysts.

Experiments are in progress to study the oxidation of higher hydrocarbons, such as hexane and cyclohexane.

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