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High yields of olefins and hydrogen from decane in short contact time reactors: rhodium versus platinum

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Abstract

The partial oxidation of n-decane to produce H_2, ethylene, and α-olefins has been compared over Rh and Pt in autothermal reactors at short contact times. Over Rh it is shown that the addition of an alumina wash coat and small foam pore size give higher H_2 selectivity ($> 85\%$), while the absence of wash coat and larger pore size give more olefins (up to 60%). In contrast, Pt is unsatisfactory for producing either H_2 or olefins because the conversion of both n-decane and O_2 is lower. Pt produces essentially no H_2 ($< 0.1\%$ under any conditions). Ignition and autothermal operation over Pt also occur only over a narrow range of composition and flow rate. A catalyst consisting of Pt–Rh gave higher olefin selectivity (89%) than either metal, while producing little H_2. We interpret these results as caused by the high activity of Rh that removes all O_2 early in the catalyst, leaving homogeneous pyrolysis to produce olefins. The lower activity of Pt appears to be caused by its inability to completely dissociate n-decane, leaving fragments on the surface that inhibit reaction and produce a less active surface.

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Keywords: Olefins; Decane; Platinum; Rhodium; Ethylene; Hydrogen; Millisecond reactor; Monolith; Autothermal

1. Introduction

The partial oxidation of lower alkanes (methane, ethane, and propane) produces syngas ($H_2 + CO$) with $> 90\%$ selectivity at $> 80\%$ fuel and oxygen conversion. This process occurs readily over Rh on low area ceramic foam monoliths at short contact times. It operates autothermally from 700 to 1000 °C using a fuel to oxygen ratio of $C/O \sim 1$ [1–6]. Over Pt and Pt–Sn this process can be made to produce olefins with up to 85% selectivity to ethylene from ethane at $C/O \sim 2$ [7].

We have recently shown that liquid alkanes such as n-decane and n-hexadecane can be converted to H_2 and CO with $> 80\%$ selectivities over Rh by using a fuel injector for rapid heating and mixing with air without ignition of the mixture. When using n-hexadecane at $C/O \sim 2$ this Rh catalyst gave $\sim 84\%$ selectivity to olefins [8]. Further, these olefins can be tuned between ethylene and higher α-olefins by adjusting the C/O feed ratio and flow rate. Fuel mixtures such as diesel fuel were also successfully reformed at high selectivities and conversions [8].

In this paper we compare the partial oxidation of n-decane over Rh and Pt surfaces. We examine in more detail the effects of wash coat and foam pore size to determine how these variables affect the yields of products. We find dramatic differences between the metals, especially between their ability to form H_2 and olefins.

2. Experimental

The apparatus and procedure have been described in detail previously [8]. An automotive fuel injector sprayed fuel droplets into a reactor tube. The reactor is heated from the wall to ∼ 250 °C. The fuel is mixed with room temperature air that flows around the injector. This creates a temperature and concentration gradient which keeps the fuel–air composition outside the flammable range to avoid flames and pyrolysis before the catalyst. The air flow was controlled by mass-flow controllers and the fuel flow by electronic control of the injector.

Catalysts were ceramic alumina foams 18 mm diameter and 10 mm long sealed into the quartz reactor tube with Fiberfrax alumina–silica paper. Products were analyzed with a dual-column gas chromatograph capable of detecting all species from H_2 to n-decane.

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Foams with 45 and 80 pores per linear inch (ppi) were compared. For some experiments these were coated with ∼ 5 wt% γ-Al_2O_3 to roughen the catalyst surface and increase its surface area [9]. The coating was performed by soaking the monoliths in a γ-Al_2O_3 slurry and then drying under vacuum and calcining for ∼ 4 h at 600 °C. Monoliths with or without wash coats were then coated with either Rh or Pt by soaking them in $Rh(NO_3)_3$ or H_2PtCl_6 solutions and calcining for ∼ 6 h at 600 °C. Pt–Rh alloys were made by mixed solutions of the two salts.

All experimental data were repeated several times on a given catalyst for operating times of many hours. Most results were performed on several samples prepared identically. All results were repeatable within at least 1% between experiments and 2% between samples. We observed no activation or deactivation on any catalyst over 50+ h of continuous and intermittent operation. Presumably, such high metal loading allows the formation of large size particles due to sintering. These large particles can resist further sintering, which accounts for the catalyst durability. Stability tests of thousands of hours of operation are required to assess the commercial feasibility of the process.

In all the experiments surface carbon was periodically removed from the catalysts by turning off the fuel to oxidize it in pure air. This produced an exotherm of up to several hundred degrees that lasted for ∼ 20 s, especially after operation at a high C/O feed ratio. The subsequent activity and selectivity were unaffected by carbon burnoff. We will discuss measurement of carbon on the catalyst by burnoff transients and mass spectrometer measurement of CO and CO_2 production in a later paper. These experiments show that up to 10 wt% carbon can be deposited on the catalysts during operation with n-decane at high C/O, but this produces no detectable deviations from steady-state performance or deactivation.

In all experiments the total selectivity to all alkane products was $< 5\%$ (not shown), and these were mostly CH_4 with small amounts of C_2H_6 and C_3H_8. The alkane selectivity increased with the C/O feed ratio and became $< 0.1\%$ at $C/O < 1$.

3. Results

In these experiments n-decane and air were fed to the monolith reactor at vapor flow rates of 2 and 4 SLPM (standard liters per minute), which correspond to catalyst contact times of 24 and 12 ms, respectively, at an average catalyst temperature of 800 °C. The C/O feed ratio was typically varied from 0.6 to 2.0. The reactor pressure was just above 1 atm. The wall temperature was 250 °C, which is above the boiling point of n-decane (174 °C) and above its autoignition point (200 °C). For n-decane the combustion ratio is $C/O = 0.323$, the syngas ratio is $C/O = 1$, and the ratio that gives the highest selectivity to olefins is $C/O \sim 2$.

3.1. Rhodium

We examined the effects of flow rate, wash coat, and pore size using Rh-coated monoliths. Fig. 1 shows the conversion of n-decane and oxygen and the catalyst back-face temperature (top), the product distribution (middle), and the major olefin products (bottom) at total vapor flow rates of 2 and 4 SLPM. The catalyst was an 80 ppi α-Al_2O_3 monolith, wash coated with ∼ 5 wt% of γ-Al_2O_3, and then coated with ∼ 2 wt% Rh. The oxygen conversion was $> 99\%$ for all ratios and flow rates. The n-decane conversion was $> 99\%$ for $C/O < 1.2$ at 4 SLPM and it decreased to 80% as the feed became more fuel rich. At 2 SLPM the n-decane conversion decreased from 95 to 25% as the feed became more fuel rich. The catalyst back-face temperature increased with increasing flow rate because at higher flow rates the rate of heat generation increases, causing the reactor to operate closer to adiabatic. As expected, the catalyst back-face temperature decreased as the fuel conversion decreased.

The optimum yield in both H_2 and CO for all flow rates occurred at $C/O = 0.8$, a ratio slightly lower than syngas stoichiometry. The highest selectivities for H_2 (86%) and CO (84%) occurred at $C/O = 0.8$ and 4 SLPM. The combustion products increased as the feed ratio approached the combustion stoichiometry.

The syngas selectivity decreased and the olefin selectivity increased as the feed became fuel rich. The olefin products consisted of almost exclusively α-olefins as described previously [8], with the highest selectivity of ∼ 60% at 8 SLPM. The major olefin produced was ethylene with 36% selectivity at $C/O = 1.0$ and 8 SLPM. The ethylene selectivity dropped at both leaner and richer ratios.

The effect of a γ-Al_2O_3 wash coat on a 80 ppi α-Al_2O_3 catalyst support is shown in Fig. 2. The graphs on the left show the results of a γ-Al_2O_3 wash coated 2 wt% Rh catalyst and the ones on the right show those with 2 wt% Rh without wash coat. The conversion of n-decane and oxygen and the catalyst back-face temperature (top), the product distribution (middle), and the olefin products at 4 SLPM are shown in detail at the bottom. The oxygen conversion increases from > 95 to $> 98\%$ at all C/O feed ratios when no wash coat is added. The fuel conversion was approximately the same in both cases, decreasing from 98% at $C/O < 1.2$ to 82% at $C/O = 2$. The catalyst back-face temperature was ∼ 100 °C higher at all C/O feed ratios without wash coat.

The wash-coated catalyst shows a slightly higher (∼ 5%) maximum in the H_2 and CO selectivity. The highest syngas selectivity occurred at $C/O = 0.8$ in both cases. As the C/O feed ratio increased, the syngas selectivity decreased and the α-olefin selectivity increased. The maximum α-olefin selectivity was 29% in the wash-coated catalyst and 40% without wash coat. The major olefin produced was ethylene with a maximum selectivity of 12% in the wash-coated catalyst and 24% without wash coat, and both maxima occurred at $C/O = 1$.

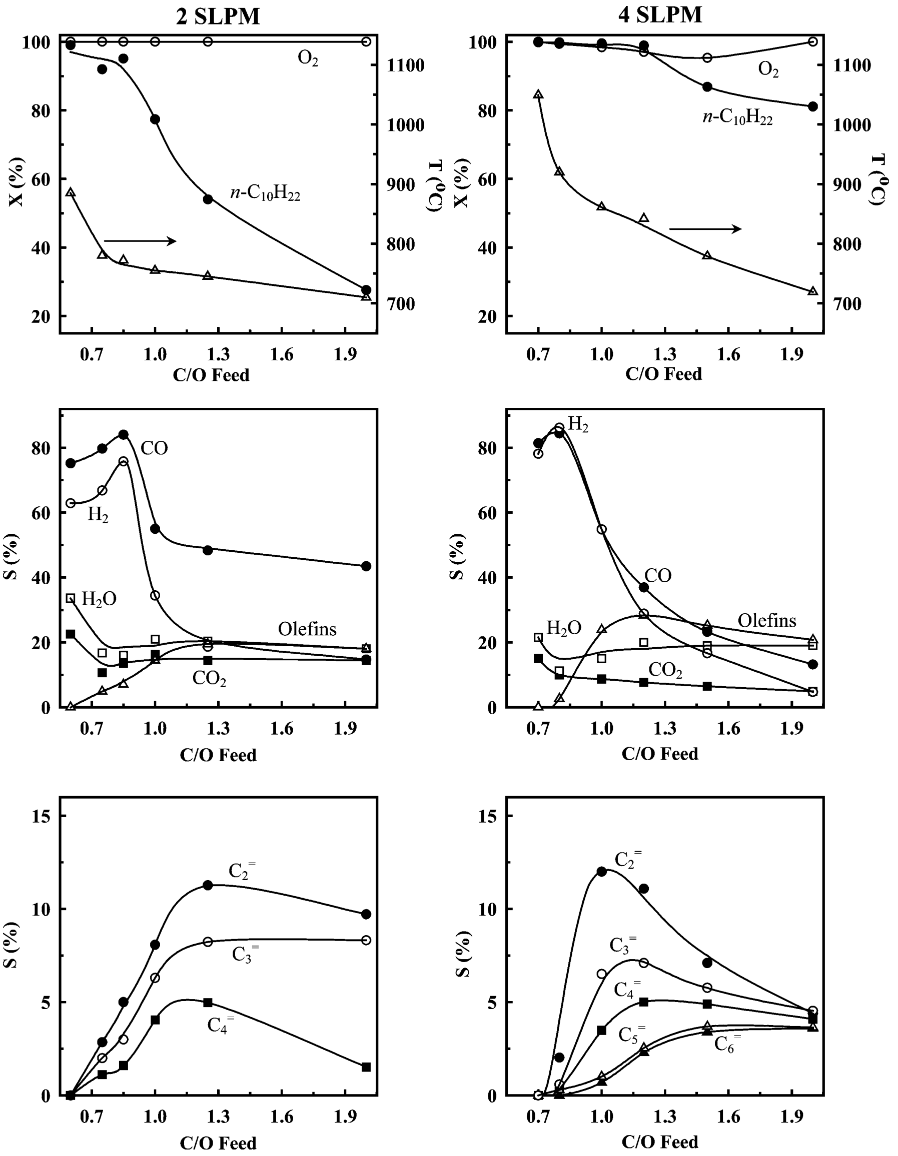

Fig. 1. Effect of the n-decane/oxygen feed ratio on the reactants conversion and catalyst back-face temperature (top), the product selectivity (middle), and the small olefins (bottom) over Rh catalysts.

The performance of a 45 ppi (left) catalyst support and an 80 ppi (right) with 2 wt% Rh are shown in Fig. 3. The conversion of n-decane and oxygen and the catalyst back-face temperature (top), the product distribution (middle), and the major olefin products (bottom) at 4 SLPM are shown. The 45 ppi catalyst showed lower oxygen conversion, decreasing from 100 to 93% as the C/O ratio increased. The oxygen conversion in the 80 ppi catalyst was $> 99\%$ at all C/O ratios. The n-decane conversion was 96% for the 45 ppi catalyst and $> 98\%$ for the 80 ppi catalyst at $C/O < 1.2$, and they both decreased to $\sim 80\%$ as the feed became fuel rich.

The maximum hydrogen selectivity was higher for the 80 ppi catalyst, 81% versus 69%. The maximum CO selectivity was also higher for the 80 ppi catalyst, 79% versus 69%. The syngas selectivity dropped and the olefin selectivity increased as the feed became fuel rich ($C/O > 1$). The olefin products consisted of almost exclusively α-olefins, and the highest selectivity was 40% for the 80 ppi catalyst and 78% for the 45 ppi catalyst. The highest selectivity to ethylene was 24% for the 80 ppi catalyst and 37% for the 45 ppi catalyst, they both occurred at $C/O \sim 1.0$.

3.2. Platinum

Autothermal operation of Pt could be obtained only over a narrow range of composition and flow rate. At C/O feed ratios of < 0.8 safe operation was jeopardized by the high catalyst temperature and the low oxygen conversion, while ratios > 1.2 resulted in unstable operation and extinction. At flow rates > 4 SLPM the oxygen conversion became dangerously low, and at < 2 SLPM it was difficult or impossible to ignite the catalyst.

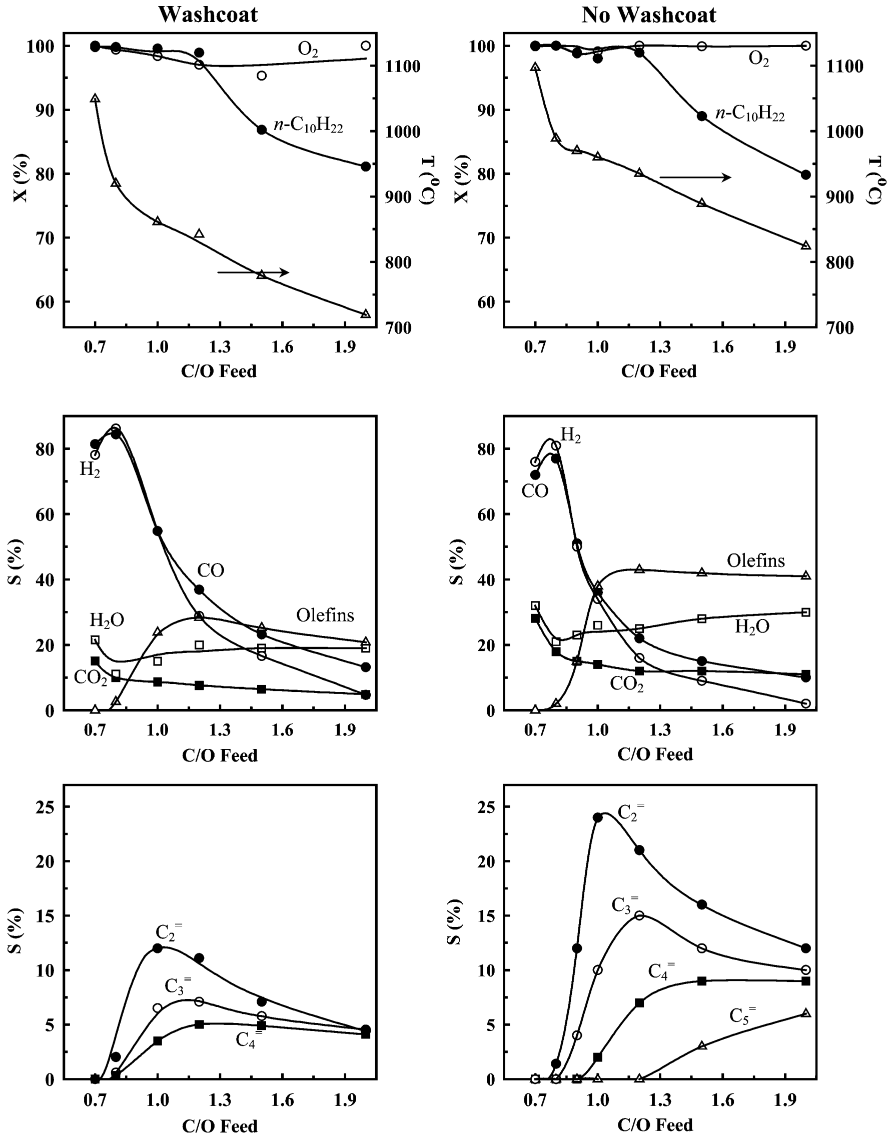

Fig. 2. Effect of the γ-Al_2O_3 wash coat. The effect of the n-decane/oxygen feed ratio on conversions (top), and the product selectivity (middle and bottom) over Rh catalysts at 4 SLPM.

Fig. 4 shows the conversion of n-decane and oxygen and the catalyst back-face temperature (top), the product distribution (middle), and the major olefin products (bottom) at vapor flow rates of 2 and 4 SLPM. The catalyst was an 80 ppi α-Al_2O_3 monolith coated with 2 wt% Pt.

The range of C/O examined over Pt was much lower than for Rh because oxygen conversion was low at all C/O feed ratios and flow rates, ~ 75% at 2 SLPM and ~ 45% at 4 SLPM. The n-decane conversion was ~ 80% for both 2 and 4 SLPM. The catalyst back-face temperature decreased with increasing flow rate because of the decrease in oxygen conversion. As expected, the catalyst back-face temperature decreased as the fuel conversion decreased.

The selectivity to H_2 was undetectably small on Pt at all C/O feed ratios and flow rates; we placed a bound on this of 0.1%. The selectivity to CO at all C/O feed ratios was also much lower than over Rh, ~ 12% at 2 SLPM and ~ 9% at 4 SLPM. The selectivity to H_2O was high, ~ 50% at 2 SLPM and ~ 40% at 4 SLPM, and did not change as the feed became fuel rich. The combustion products increased slightly as the feed ratio approached the combustion stoichiometry. The olefin products consisted of almost exclusively α-olefins, and the highest selectivity of 88% occurred at 4 SLPM. The major olefin produced was ethylene with 13% selectivity at $C/O = 0.8$ and 2 SLPM. At 4 SLPM the selectivity to ethylene was ~ 5%.

3.3. *Alloy catalysts*

To examine the effects of Pt–Rh alloys we used an 80 ppi α-Al_2O_3 monolith coated with ~ 2 wt% Pt–Rh at the ratio of

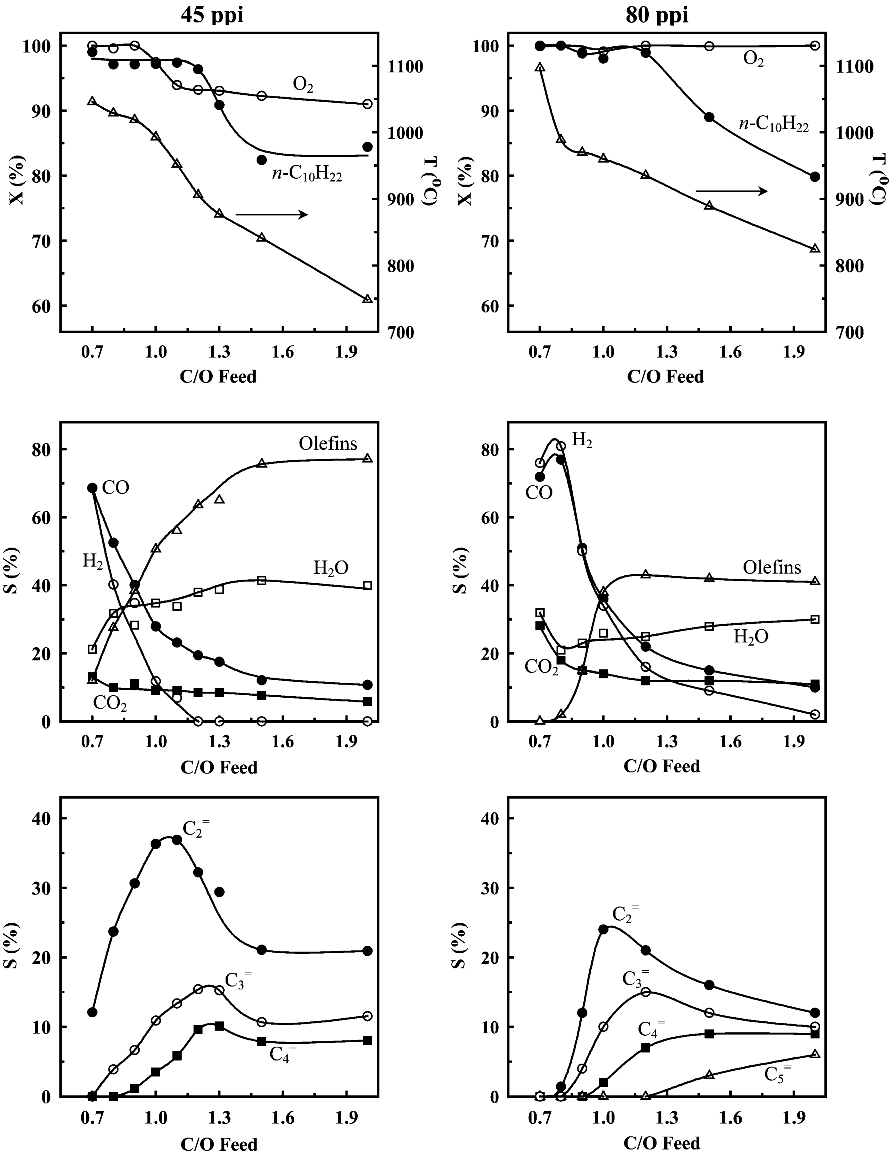

Fig. 3. Effect of the catalyst porosity 45 ppi (left) vs 80 ppi (right). The effect of the C/O feed ratio on conversions (top) and the product selectivity (middle and bottom) over Rh without wash coat at 4 SLPM.

10:1. The fuel and oxygen conversions were higher than over Pt and the catalyst operated over a wider range of C/O ratios. Fig. 5 shows the conversion of n-decane and oxygen and the catalyst back-face temperature (top), the product distribution (middle), and the major olefin products (bottom) at flow rates of 2 and 4 SLPM.

The highest selectivities for H_2 (18%) and CO (49%) occurred at $C/O = 0.7$ and 2 SLPM. The syngas selectivity dropped rapidly and the olefin selectivity increased as the feed became more fuel rich. The olefin products consisted of almost exclusively α-olefins, and the highest olefin selectivity of 81% occurred at both 2 and 4 SLPM. The major olefin produced was ethylene with 33% selectivity at $C/O = 0.9$ and 2 SLPM. The highest selectivities for propylene and 1-butene were obtained at 2 SLPM.

3.4. Pt with Rh on the front face

Experiments were attempted on a 45 ppi monolith coated with 2 wt% Pt, but it failed to ignite at any flow rate. Therefore, we coated a drop of Rh on the front face of a 45 ppi Pt-coated monolith. This corresponds to $\sim 0.002\%$ Rh in Pt.

This Pt catalyst with Rh on the front face had no problems igniting. Fig. 6 shows the results obtained at a total vapor flow rate of 6 SLPM. This catalyst shows a low oxygen conversion which decreased from 95 to $\sim 70\%$ as the C/O increased. The synthesis gas selectivity and the overall product distribution are comparable to those from the Pt–Rh 10:1 catalyst. However, total olefins selectivity is higher, almost 90%. The ethylene selectivity was also higher with a maximum of 40% at $C/O = 1.2$.

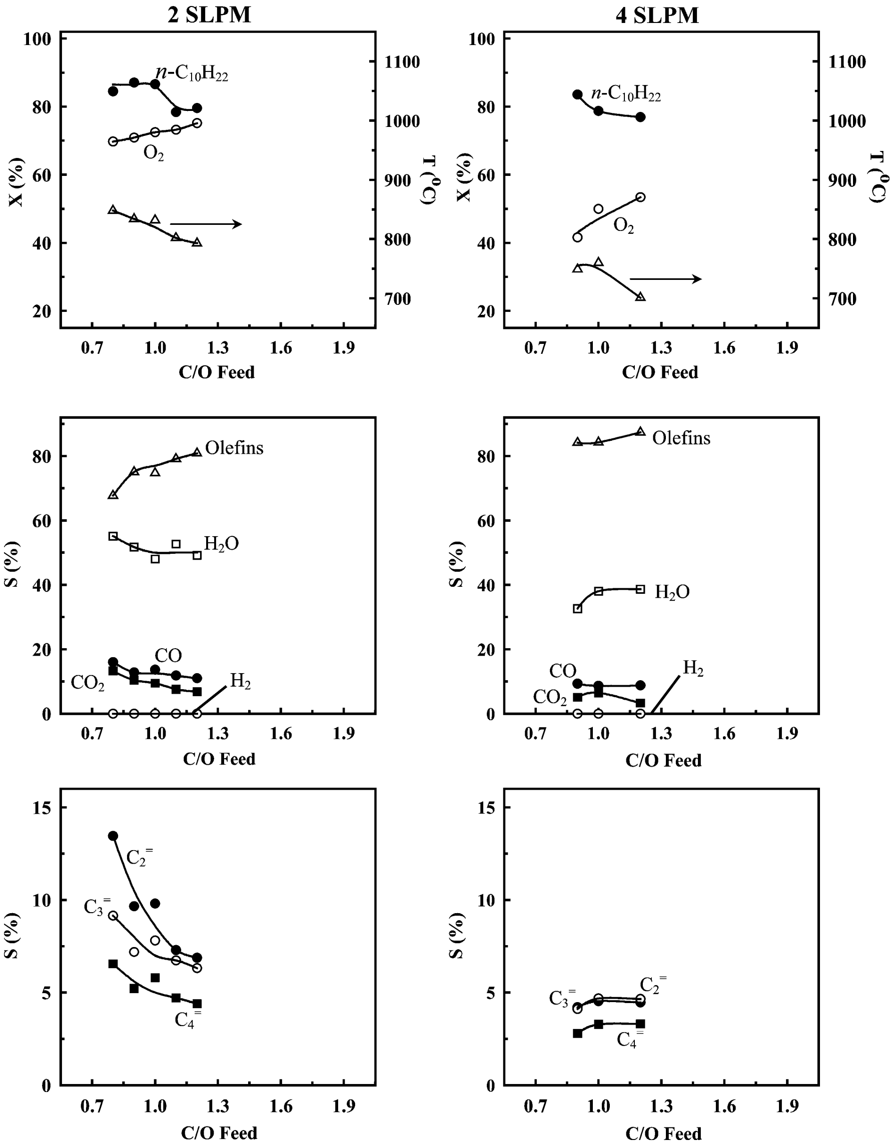

Fig. 4. Effect of the n-decane/oxygen feed ratio on conversions and catalyst back-face temperature (top) and the product selectivity (middle and bottom) over Pt catalyst. It operates over a narrow C/O range and shows low fuel and oxygen conversions. It was also difficult to ignite.

3.5. Downstream reactor temperature

The products are collected ~ 15 cm downstream of the catalyst. The products leave the catalyst at a high temperature, but they cool down somewhat before they are collected for analysis. Previous experiments showed that from ethane, considerable downstream homogeneous reaction results in a higher ethylene yield [7].

We added or removed insulating material downstream of the catalyst to control the temperature of the gases after the catalyst. A thermocouple was introduced ~ 15 cm downstream of the catalyst, to measure the exit gas temperature. We found that increasing the gases temperature, on a Rh catalyst, by ~ 200 °C can significantly increase fuel conversion and olefins selectivity. Fig. 7 shows the yield (yield = fuel conversion × selectivity) of olefins and ethylene obtained with and without heating. At high C/O feed ratios the higher temperature case shows a much larger yield to olefins, which confirms that the higher temperature sustain homogeneous chemistry downstream of the catalyst.

4. Discussion

The most surprising feature of these experiments is the low reactivity of Pt compared to Rh for n-decane and the complete absence of H_2 production over Pt. This is not expected from comparable experiments with lower alkanes. We will discuss reasons for these differences and the mechanisms they imply.

4.1. Mechanism

Basically, the mechanism for syngas production that we and others have proposed [2,3,10] assumes that the process

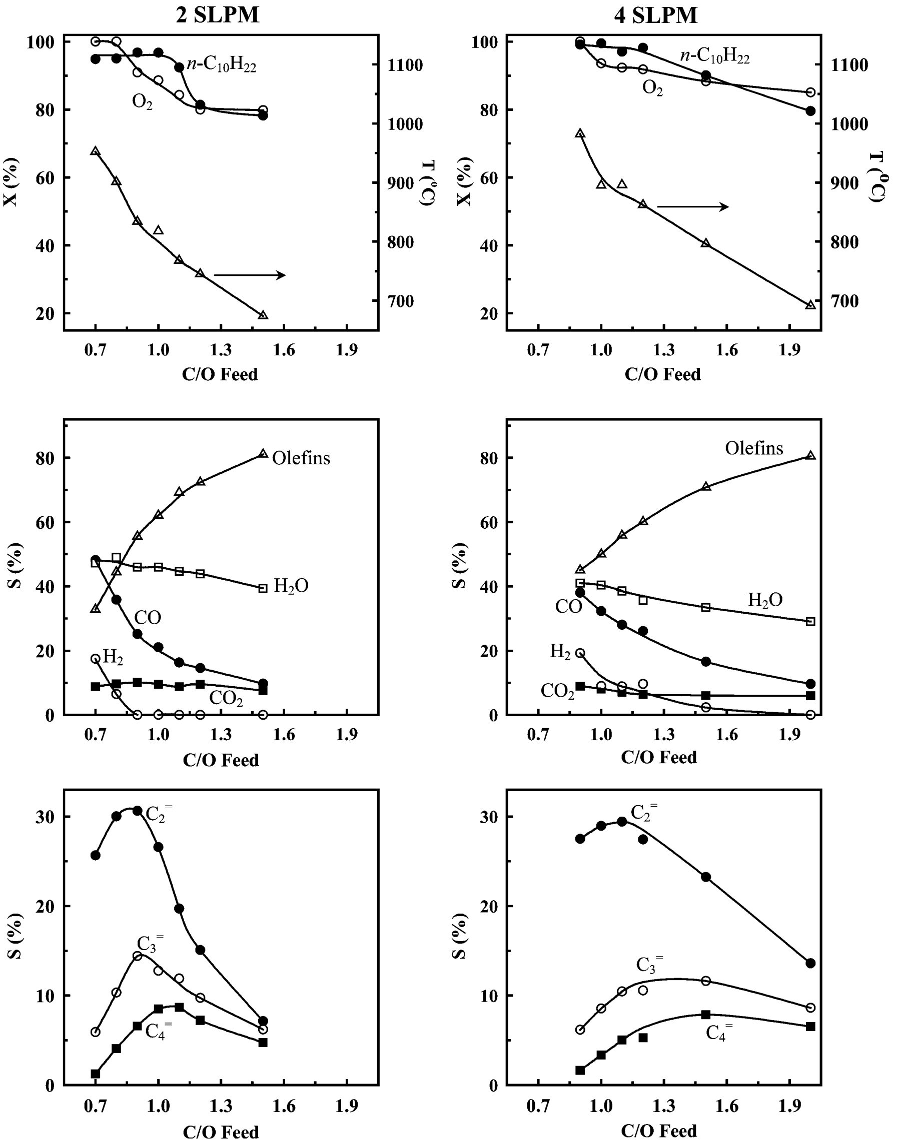

Fig. 5. Effect of the n-decane/oxygen feed ratio on conversions and catalyst back-face temperature (top), the product selectivity (middle), and the small olefins (bottom) over uniformly coated Pt:Rh 10:1 catalyst.

is initiated by dissociation of the alkane followed by rapid oxidation of C on the surface to form CO and dimerization of adsorbed H to form H_2. This generally occurs within the first millimeter of the Rh catalyst, as confirmed by experiments with variable bed length [11] and by detailed models [12]. The front face of the catalyst is up to 200 °C hotter than the back face. For all alkanes CO appears to be the primary product of the surface oxidation reaction. For CH_4 most reaction occurs on the surface, and less than 15% of the H_2 formed is produced by reaction of CH_4 with H_2O (steam reforming) [1,2].

Olefin formation over Pt and Pt–Sn from C_2H_6 appears to occur through initial surface combustion that rapidly heats the catalyst to temperatures where homogeneous and surface pyrolysis produce C_2H_6 [7,13]. Downstream sampling of products from C_2H_6 on Pt confirms that considerable reaction occurs homogeneously after the gases have left the catalyst [7,14]. Addition of D_2 to the feed shows that little deuterated ethylene is formed [7], further indicating the simplicity of the mechanism at short contact times.

Higher alkanes of course have many more reaction channels than CH_4 and C_2H_6. Pyrolysis of normal alkanes occurs by β-scission and β-H elimination, which produces ethylene and α-olefins, respectively [8].

4.2. Rhodium

Over Rh, the experiments suggest that all alkanes are initially dissociated completely to C and H, and that partial or total oxidation of these species removes them from the surface (with microsecond to nanosecond surface residence times), and this provide the energy to heat the catalyst to ~ 1000 °C to initiate pyrolysis which may be largely homogeneous. The Rh catalysts therefore have an oxidation zone

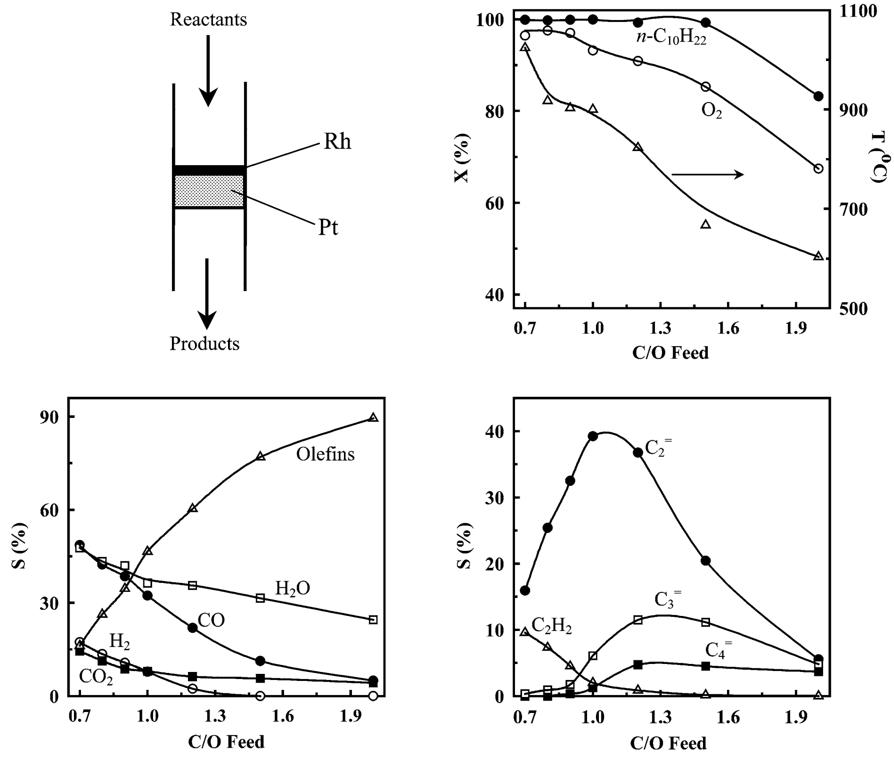

Fig. 6. Effect of the n-decane/oxygen feed ratio on conversions and catalyst back-face temperature (top), the product selectivity (bottom left), and the olefin distribution (bottom right) over a 2 wt% Pt catalyst with 0.002 wt% Rh on the front face. The catalyst cross section is shown on the top left.

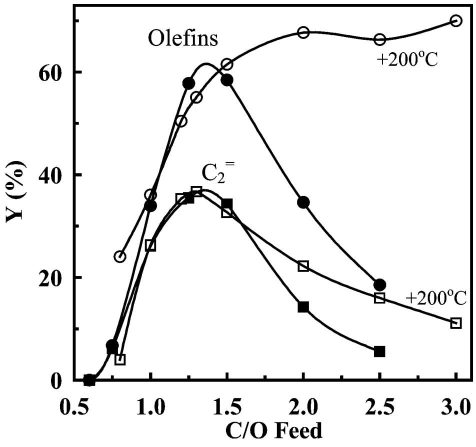

Fig. 7. Effect of the reactor downstream temperature on total olefin and ethylene yields at 8 SLPM over Rh catalysts. It clearly shows that increasing the gases temperature downstream of the catalyst results in a significant increase in ethylene and olefin yield. These results emphasize that homogeneous reactions take place after the catalyst.

comprising the first millimeter of the catalyst where O_2 and adsorbed O maintain a carbon-free surface. After all O_2 is consumed, C builds up sufficiently to slow surface chemistry and allow pyrolysis to dominate. However, multilayers of carbon and graphite would block the catalytic surfaces and block channels, and this would clearly be unsatisfactory. The reasons for the fact that this process still functions with up to 10 wt% carbon in the ceramic foam are still not well understood.

All of these catalysts produced primarily α-olefins, with very little internal olefins or chain branching. This shows that intermolecular chain transfer, which would produce isomerization and internal olefins, is not important. In the short time of these experiments, unimolecular β-scission and H elimination appear to dominate over all bimolecular reactions.

4.3. Effect of wash coat and pore size

The α-Al_2O_3 foam monoliths are usually wash coated with ~ 5 wt% of γ-Al_2O_3 in order to increase surface area and decrease pore size. This technique is assumed to work best when mostly heterogeneous reactions are desired [9]. We studied the effect of a γ-Al_2O_3 wash coat on a 80 ppi Rh-coated catalyst. As shown in Fig. 2, the γ-Al_2O_3 wash coat improves synthesis gas selectivity by ~ 5%. However, the catalyst without wash coat shows 25% higher selectivity to olefins. The fuel and oxygen conversions were comparable, but the catalyst back-face temperature was ~ 100 °C higher in the catalyst without wash coat. These results are presumably due to the lower surface area that accounts for less heterogeneous chemistry, thus allowing more of the reactants to produce olefins homogeneously.

The effect of pore size was compared over Rh-coated 45 and 80 ppi monoliths. As shown in Fig. 3, fuel and oxygen conversions and catalyst back-face temperature were lower on the 45 ppi catalyst than on the 80 ppi. The selectivity to synthesis gas was also lower on the 45 ppi catalyst but, the

Table 1
Maximum selectivity (%) of products from different fuels over Rh, Pt, Pt–Rh 10:1 or Pt with Rh on the front face catalysts

	H_2			CO			Total olefins			C_2H_4		
	Rh	Pt	Pt–Rh	Rh	Pt	Pt–Rh	Rh	Pt	Pt–Rh	Rh	Pt	Pt–Rh
n-$C_{10}H_{22}$[a]	86	0	18 (10)	84	12	49 (50)	60	88	81 (89)	36	13	33 (40)
CH_4	95	84	–	94	93	–	–	–	–	–	–	–
C_2H_6	70	40	–	70	63	–	–	–	–	40	80	–
C_3H_8	82	40	–	80	68	–	12	60	–	8	30	–
n-C_6H_{14}	99	–	–	96	–	–	15	–	–	7	–	–
n-$C_{16}H_{34}$	82	–	–	81	–	–	84	–	–	8	–	–

Totals greater than 100% because maximum occur at different conditions. Numbers in parentheses are for a 2 wt% Pt catalyst with 0.002 wt% Rh on the front face. Total olefins include ethylene.

[a] Current results.

selectivity to olefins almost doubled and the selectivity to water was ∼ 30% higher on the 45 ppi catalyst. These results can be attributed to the larger pore size of the 45 ppi (∼ 350 µm for the 45 ppi versus ∼ 200 µm for the 80 ppi), which allows more homogeneous chemistry to take place, thus increasing the selectivity to olefins. The wash coat and pore-size effects observed in these experiments are consistent with those previously found with hexane and isooctane [5].

4.4. Rhodium versus platinum

The results obtained indicate that Rh surfaces are much more active than Pt. Over Pt surfaces, the oxygen conversion was only ∼ 75% at 2 SLPM and it was so low at 5 SLPM that experiments were unsafe. Fuel conversion and catalyst temperatures were also lower over Pt than Rh surfaces. These results are summarized in the first row of Table 1 which shows maximum selectivities to these products. We note that these were obtained in air, but under different conditions of composition and flow rate.

Large differences in the product distributions exist. Rh produced hydrogen with high selectivities, while Pt made virtually zero hydrogen. The total olefins produced over Pt were larger than those over Rh under identical conditions. Over Pt the olefins were mostly 1-pentene and higher, while over Rh 1-butene and lower. Pt also produced more H_2O than Rh.

These results, in which Rh shows better reactivity than Pt, show some correlation with previous results found on smaller alkanes, but differences for decane are larger. Table 1 shows maximum selectivities to H_2, CO, total olefins (including ethylene), and ethylene for different fuels over Rh, Pt, Pt–Rh, and Pt with Rh on the front face catalysts [4,5,7,8,11,15,16]. In all alkanes studied, Pt shows a lower selectivity to synthesis gas than Rh. However, the selectivity to olefins over Pt is far greater than that over Rh. The selectivity to ethylene varies depending on the chain length of the fuel. Smaller alkanes (ethane and propane) produce more ethylene on Pt than on Rh, but large alkanes (n-decane) do the opposite. We emphasize that these are maximum selectivities observed in air under different conditions.

For n-decane the selectivity to olefins increases in the following catalyst order: Rh $\geqslant$ Pt–Rh $\geqslant$ Pt. However, the selectivity to H_2, CO, and ethylene increases in the opposite catalyst order. On methane, ethane, and propane, the selectivity to H_2 and CO increases as the catalyst changes from Pt to Rh, but the selectivity to ethylene increases in the opposite direction.

The partial oxidation of methane shows that both oxygen and fuel conversions are lower on Pt than on Rh, and the selectivity to H_2 and CO is higher on Rh than on Pt catalysts [17]. This trend can be due to a higher reactivity of surface oxygen with dissociated hydrogen over Pt than over Rh, which forms hydroxyl groups (and therefore water). This reactivity difference can be attributed to the higher bond strength for Rh–O than for Pt–O, 70 versus 52 kcal/mol (from activation energies for oxygen desorption) [3].

4.5. Alloy catalysts

The results over Pt–Rh catalysts (Table 1) indicate that this catalyst behaves like a Rh catalyst at low C/O feed ratios, although it showed much lower synthesis gas selectivity and higher olefin selectivity. At high C/O feed ratios the catalyst behaves like a Pt catalyst, producing essentially no hydrogen and large amounts of olefins and water, but with higher fuel and oxygen conversions than Pt. These results confirm the higher reactivity of Rh. A catalyst containing only ∼ 10% Rh in Pt can act as a pure Rh catalyst under certain conditions.

5. Summary

Rh and Pt catalysts for partial oxidation of larger alkanes behave quite differently than for CH_4 and C_2H_6 fuels in formation of both syngas and olefins. In formation of H_2, Pt produces essentially none under any conditions (except by adding Rh). The choice of metal is thus nearly an on–off switch for H_2. This appears to be caused by the presence of O_2 over Pt throughout and downstream that rapidly oxidizes any H_2 that might be formed in alkane pyrolysis.

Rh is also the preferable pure metal for olefin formation, and it can be tuned by geometric effects (pore size, wash coat, preheat and postheat, flow rate, and composition) with sufficient sensitivity that considerable control over a large scale process should be possible.

The results with Pt–Rh mixtures also suggest that there are chemical variables that may be tuned to optimize these processes. Other additives such as base metals and oxides should change the chemistry to enhance formation of one species and suppress others.

The geometrical and chemical causes of these changes are not simple because it involves indirect variables such as the catalyst temperature, coverages of species such as carbon, and flow patterns within the catalyst structure. The variations of these parameters with position in the catalyst are also significant. As examples, the temperature is measured to vary by 200 °C from front to back, and the coverage is calculated to switch from O to C within a few millimeters of the entrance. Both further experiments and simulations will be necessary to interpret these effects.

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