A Comparison of the Catalytic Partial Oxidation of C_1 to C_{16} Normal Paraffins

G. J. Panuccio, B. J. Dreyer, and L. D. Schmidt
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

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The catalytic partial oxidation (CPO) of C_1 through C_{16} normal alkanes is examined on Pt and Rh-coated α-Al_2O_3 ceramic foam supports. New data for heavy liquid fuels ($\geq C_6$) are combined with previously reported data for lighter hydrocarbons to explore the effects of reactant fuel molecular weight, catalyst metal, and support structure on the CPO of normal paraffins. These results show that, independent of catalyst metal and support geometry, fuel conversion and the total selectivity to olefin products increase with increasing chain length of the reacting fuel. Conversely, the selectivities of H_2 and CO decrease with increasing molecular weight of the reacting fuel. Pt catalysts generate higher selectivities to ethylene and other olefins than Rh catalysts, but Rh is the better catalyst for synthesis gas (H_2 + CO) production. Catalyst supports with lower internal surface area to volume ratio produce lower selectivities of H_2 and CO and higher selectivities of H_2O, ethylene, and other olefins than high surface area to volume catalysts. © 2006 American Institute of Chemical Engineers *AIChE J*, 53: 187–195, 2007

Introduction

Catalytic partial oxidation (CPO) is emerging as an alternative process for producing high-value chemicals such as hydrogen or olefins. CPO is a process by which vaporized hydrocarbon fuel and oxygen are reacted over a noble metal catalyst to form high selectivities of either syngas (H_2 + CO) or olefins. The most widely used industrial methods for producing hydrogen (steam reforming) and olefins (steam cracking) require large furnaces to drive the endothermic reactions.[1,2] Because these processes are limited by the rate of heat flux from the furnace to the tubular reactor, long residence times on the order of 0.1–1 s are required. Furthermore, the furnace can produce harmful pollutants such as NO_x and the reactor must be periodically shut down to remove coke from the catalyst. Because the overall reaction for CPO is exothermic, there is no need for bulky furnaces, which eliminates NO_x emissions and reduces residence times to approximately 3–10 ms.

Correspondence concerning this article should be addressed to L. D. Schmidt at schmi001@umn.edu.

There are several variables to consider within the CPO process that can determine the characteristics of the reactions taking place. Given that industrial raw materials such as natural gas and petroleum-derived feedstocks are complex mixtures of linear and branched alkanes, alkenes, and aromatics, one of the most important factors to understand is the behavior of the CPO system in relation to the reacting fuel. The first step in successfully designing a process for a fuel that is a complicated mixture is to understand how the components of that mixture behave separately. To this end, a wide variety of fuels have been reacted in CPO reactors including normal alkanes ranging from methane to *n*-hexadecane,[3–12] branched alkanes such as *i*-butane and *i*-octane,[10,13,14] and cyclic fuels such as cyclohexane.[9,14] Results show that each of these different classes of compounds behaves differently in the CPO system. In this work, we focus on the reaction of linear alkanes and describe the effect of chain length on experimental product selectivities, fuel conversions, and catalyst temperatures.

A variety of metals have been used to catalyze the partial oxidation reactions, including (but not limited to) rhodium, platinum, nickel, iridium, and palladium. Previous results on lighter alkanes have shown that Rh catalysts give the best performance for syngas production, whereas reactions on Pt giver higher

selectivities to olefins, water, and carbon dioxide.[4,6,8,15] The other metals have shown poorer performance than that of Rh and Pt because of coking, sintering, or inactivity.[4,8,13] For this reason, this work focuses on examining the effects of Rh and Pt catalysts on the CPO process for normal alkanes.

The third parameter explored in this work is the effect of the catalyst support geometry. Honeycomb monoliths, foam monoliths, sphere beds, and wire gauze have all been previously studied in the millisecond contact time catalytic partial oxidation process. Each of these supports has its own advantages. For example, honeycomb monoliths have a very regular geometry and are good supports to use for modeling experimental results and developing reaction mechanisms.[16] Wire gauzes have very rapid quenching times and so they can generate significant quantities of oxygenates from alkanes.[17,18] Foam monoliths and sphere beds have highly interconnected pore structures that improve radial mixing and heat transfer and therefore give the best overall performance in terms of syngas (or olefin) production and fuel conversion.

In this work, we focus on α-Al_2O_3 foam monoliths because they have the largest amount of data in the literature for lighter alkanes that can be used for comparison purposes. Specifically, we compare experiments performed on 80 pores per linear inch (ppi) monoliths that are prepared with a γ-Al_2O_3 washcoat to 45 ppi foams that have no washcoat. The 80 ppi foams have a smaller average pore diameter ($\sim$250 μm) than the 45 ppi supports ($\sim$470 μm) and thus have a higher ratio of geometrical surface area to foam volume ($\sim$130 cm^2/cm^3 for 80 ppi and $\sim$70 cm^2/cm^3 for 45 ppi).[19] The addition of a washcoat to the 80 ppi support roughens the surface and further decreases the pore size.[5] Comparison of the results of the experiments performed on these two different supports gives insight into the relationship between heterogeneous and homogeneous chemistry in the CPO process.

Experimental

The materials and methods for these experiments were previously described in detail elsewhere.[5,11,20] The catalyst was a 17 mm diameter, 10 mm length α-Al_2O_3 ceramic foam monolith with either 80 or 45 ppi that was coated with 5 wt % Rh or Pt metal. The catalysts were prepared by the dropwise addition of the aqueous metal salt solution ($Rh(NO_3)_3$ or H_2PtCl_6) onto the alumina support, drying in air, and calcining in a closed oven at 600°C for 5 h. The 80 ppi supports were also coated with a 5 wt % γ-Al_2O_3 washcoat to roughen the surface and enhance metal dispersion.[12] Four different catalysts were studied in this work: 80 ppi 5% Rh (or Pt) with 5% washcoat and 45 ppi 5% Rh (or Pt) with no washcoat.

The catalytic foam was placed between two blank α-Al_2O_3 monoliths to prevent axial radiative heat losses, wrapped in Fiberfrax® paper to prevent gas bypass, and placed inside a 19 mm ID quartz tube wrapped with insulation. A K-type thermocouple was placed between the back-face of the catalytic foam and the downstream blank heat shield to measure the temperature. The upstream portion of the tube was wrapped with a Variac-controlled resistive heating tape that served to preheat the gases and vaporize the hydrocarbon (when applicable). Gas flow rates were controlled with Brooks mass flow controllers and liquids were administered through a low-flow automotive fuel injector. Products were sampled with a gas-tight syringe and injected into an HP 5890 GC. Species flow rates were calculated from the peak areas in the resulting chromatogram using N_2 as an internal standard. Experimental carbon and hydrogen atom balances typically closed within $\pm$5%.

Table 1. Summary of Experimental Conditions for the Data Presented

Catalyst	Fuel	Flow	Oxidant	Reference
Rh 80 ppi w/washcoat	Methane	5 SLPM	30% N_2	Bodke et al.[5]
	Butane	5 SLPM	30% N_2	Bodke et al.[5]
	Hexane	4 SLPM	Air	Current work
	Octane	4 SLPM	Air	Current work
	Decane	4 SLPM	Air	Current work
	Hexadecane	4 SLPM	Air	Degenstein et al.[12]
Pt 80 ppi w/washcoat	Hexane	4 SLPM	Air	Current work
	Octane	4 SLPM	Air	Current work
	Decane	4 SLPM	Air	Current work
	Hexadecane	4 SLPM	Air	Current work
Rh 45 ppi no washcoat	Methane	5 SLPM	30% N_2	Bodke et al.[5]
	Ethane	5 SLPM	20% N_2	Huff and Schmidt[7]
	Butane	5 SLPM	30% N_2	Bodke et al.[5]
	Hexane	4 SLPM	Air	Current work
	Octane	4 SLPM	Air	Current work
	Decane	4 SLPM	Air	Current work
Pt 45 ppi no washcoat	Methane	4 SLPM	5% N_2	Torniainen et al.[4]
	Ethane	4.5 SLPM	Air	Huff et al.[6]
	Propane	5 SLPM	Air	Huff et al.[8]
	Butane	5 SLPM	Air	Huff et al.[8]
	Hexane	4 SLPM	Air	Current work
	Octane	4 SLPM	Air	Current work
	Decane	4 SLPM	Air	Current work

Results

Table 1 shows the nominal total reactant flow rate and oxidant for all the combinations of fuel and catalyst that are investigated in this study. All results that are indicated as being performed for the current work are performed at 4 standard liters per minute (SLPM at 25°C and 1 atm) total flow rate with air ($N_2/O_2 = 3.76$) as the oxidant. At a typical reactor temperature of 900°C, this flow rate corresponds to an average catalyst contact time of about 5 ms. Data acquired from the literature are as close to these conditions as is available. No data are plotted for experiments on 80 ppi Pt with washcoat catalysts for fuels lighter than hexane because the only data available in the literature are for catalysts that were not prepared with a washcoat.

Temperature

The measured catalyst back-face temperature is plotted as a function of reactant C/O ratio, catalyst metal, support geometry, and reacting fuel in Figure 1. The measured catalyst back-face temperature is not often reported in the literature for the lighter alkanes, and thus most data presented in Figure 1 were obtained as current results for liquid normal alkane fuels. There are no prevailing trends that relate reactant chain length to catalyst temperature. In general, the back-face temperature cools from a range of 1050 to 1150°C at C/O $<$ 1.0 to roughly 750 to 850°C at C/O = 2.0.

There are a few notable exceptions. On 45 ppi Rh no washcoat catalyst, the temperature measured for ethane CPO is several hundred degrees hotter than the temperatures for other fuels. This is also the case for the reaction of methane on

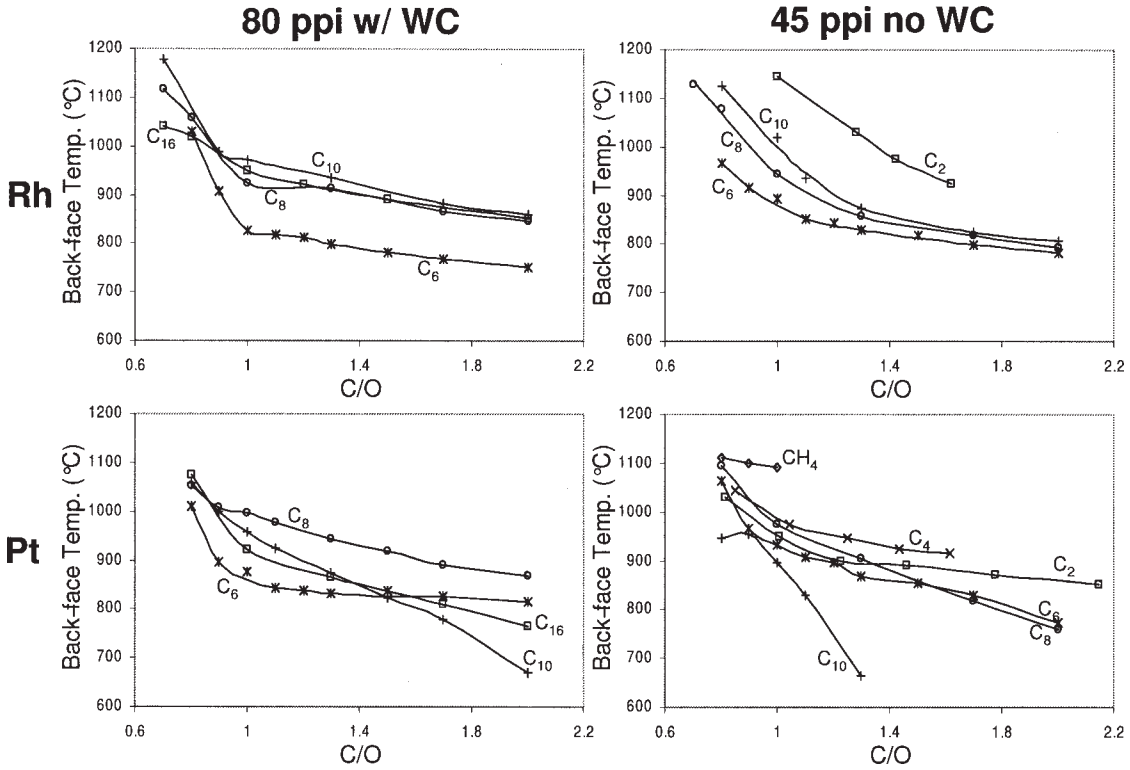

Figure 1. Measured catalyst back-face temperature for CPO of C_1–C_{16} hydrocarbons on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

45 ppi Pt no washcoat catalysts. The methane experiment was carried out in O_2 with a 5% N_2 dilution and the ethane experiment had a 20% N_2 dilution, whereas the other temperatures are obtained from reactions in air ($N_2/O_2 = 3.76/1$). The temperatures observed in the ethane and methane experiments are higher because of the absence of N_2, which acts as a diluent and a heat sink.

Fuel conversion

Fuel conversion is plotted as a function of reactant C/O ratio, catalyst metal, and support geometry for normal alkanes ranging from methane to hexadecane in Figure 2. In general, the conversion of each fuel is 100% for C/O < 1.0 and decreases as the reactant mixture becomes increasingly fuel rich. These results also show that fuel conversion increases with increasing molecular weight, independent of catalyst metal or support pore size. For example, at C/O $= 2.0$ on 80 ppi Rh with washcoat catalysts, fuel conversion increases from 45% for hexane to 91% for hexadecane. The exception to the trend is the conversion of ethane on 45 ppi Rh no washcoat catalyst where the ethane conversion is greater than that of octane but less than that of decane. This is most likely explained by the difference in the experimental conditions because the ethane CPO was conducted in only 20% N_2 (instead of air stoichiometry), which resulted in higher catalyst temperatures than that of the other fuels (see Figure 1). The increase in temperature increases reaction rates, which leads to higher fuel conversion than expected if the reaction were carried out in air.

The average pore diameter in the support structure does not have a significant effect on fuel conversion for Rh catalysts. The conversion of decane, octane, hexane, and methane is nearly the same on both 80 and 45 ppi Rh catalysts. For Pt-coated monoliths, the 80 ppi catalysts have a higher fuel conversion than that of the 45 ppi catalysts. For example, at C/O $=$ 2.0, the conversion of octane on 80 ppi Pt (85%) is greater than the conversion on 45 ppi Pt catalyst (64%).

For each of the C_6 through C_{16} liquid fuels, the conversion on 80 ppi Pt catalysts is higher than the corresponding conversion on 80 ppi Rh catalysts. For example, the conversion of hexane at C/O $= 2.0$ increases from 45% for Rh to 61% for Pt. However, on 45 ppi foams, the catalyst metal does not have an effect on the fuel conversion. The octane conversion at C/O $=$ 2.0 on 45 ppi Pt catalyst (64%) is nearly equal to the conversion on 45 ppi Rh catalyst (65%).

Syngas selectivity

Hydrogen and CO selectivities are plotted in Figures 3 and 4 as a function of catalyst metal, support geometry, reacting fuel, and feed stoichiometry. For a single fuel, syngas selectivity decreases with increasing C/O inlet stoichiometry on every catalyst studied. For example, experiments performed on 80 ppi Pt with washcoat catalysts show that the selectivity of H_2 produced from hexane decreases from 80% at C/O $= 0.8$ to 31% at C/O $= 2.0$. H_2 and CO selectivities decrease with increasing molecular weight on 80 ppi catalysts. Carbon monoxide selectivity at C/O $= 1.5$ decreases from 79% for hexane to 35% for hexadecane for experiments performed on 80 ppi Rh with washcoat catalysts. For the 45 ppi no washcoat catalysts, syngas selectivity is roughly equal for fuels heavier than ethane.

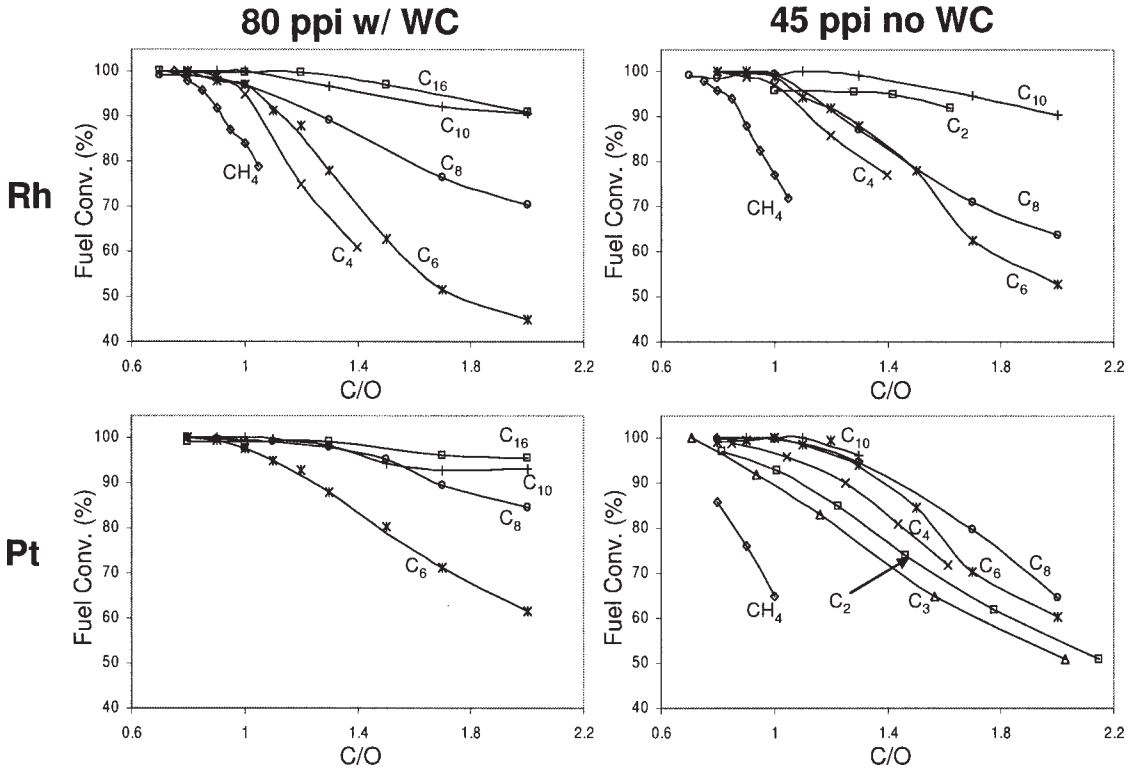

Figure 2. C_1–C_{16} fuel conversion on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

Under fuel-rich conditions (C/O > 1.0), fuel conversion increases with increasing molecular weight on all catalysts.

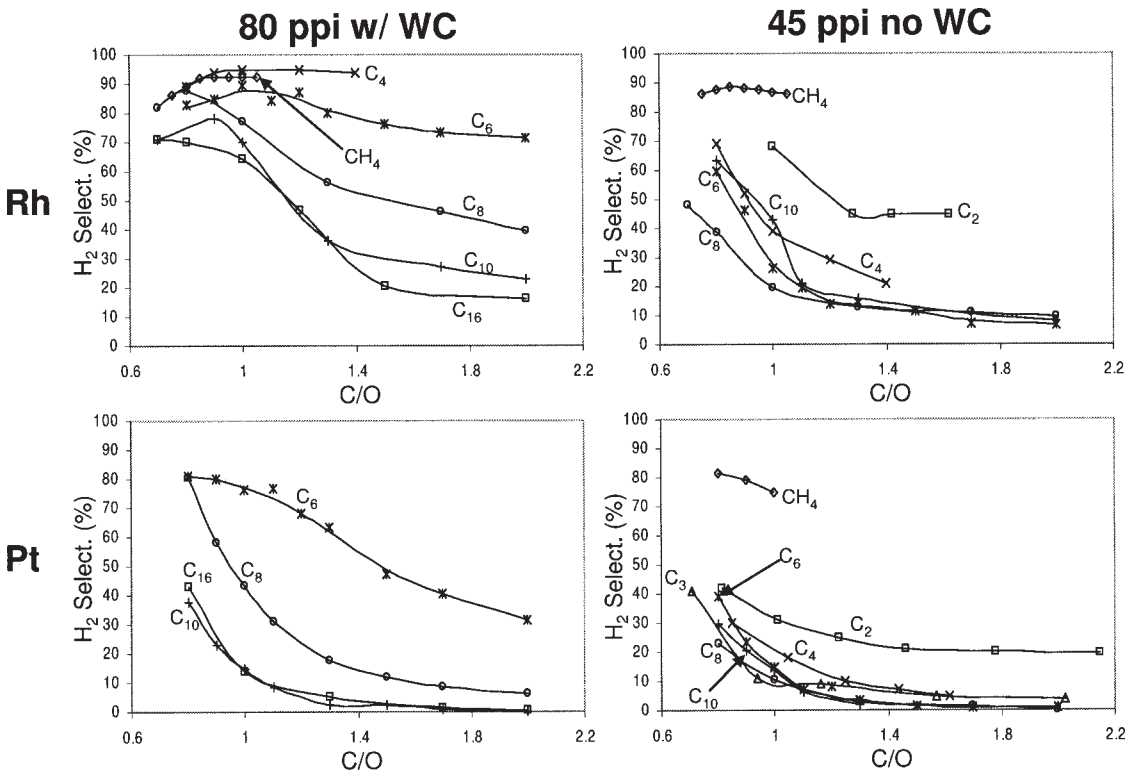

Figure 3. H_2 selectivity for CPO of C_1–C_{16} hydrocarbons on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

H_2 selectivity decreases with increasing molecular weight for experiments on 80 ppi catalysts. For 45 ppi catalysts, H_2 selectivity is approximately equal for fuels heavier than ethane.

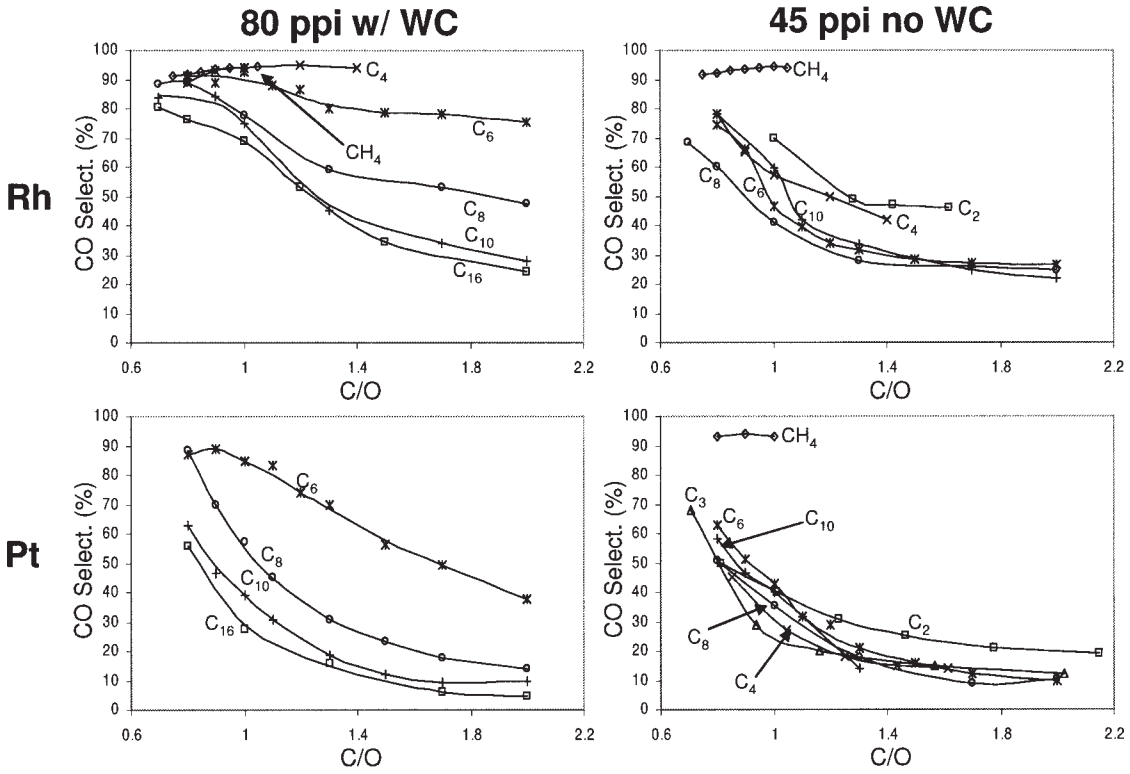

Figure 4. CO selectivity for CPO of C_1–C_{16} hydrocarbons on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

CO selectivity decreases with increasing molecular weight for experiments on 80 ppi catalysts and is approximately the same for fuels heavier than ethane on 45 ppi foams.

On a catalyst with equivalent specific surface area, experiments performed on Rh produce higher H_2 and CO selectivities than experiments performed with Pt. The CPO of octane on 80 ppi catalysts at C/O = 2.0 shows that reactions on Rh produce 39% H_2 selectivity, whereas Pt produces only 6%. Similarly, octane CPO experiments performed at C/O = 0.8 on 45 ppi foams coated with Rh produce 39% H_2 selectivity, whereas Pt gives only 23%.

For the same metal catalyst, reactions carried out on 80 ppi washcoated foams generate much higher selectivities to syngas than 45 ppi foams that are prepared without a washcoat. The CPO of decane on 80 ppi foams at C/O = 1.0 produces 75% CO selectivity, whereas 45 ppi foams produce only 47%.

Combustion product selectivity

The selectivity of H_2O is plotted as a function of inlet stoichiometry, catalyst metal, catalyst support structure, and reacting fuel in Figure 5. In general, the trends in water selectivity are the opposite of the trends for H_2 and CO selectivity. For the same metal and reacting fuel, the selectivity of H_2O is greater on 45 ppi catalysts that are prepared without a washcoat than on 80 ppi foams that are prepared with a washcoat. For example, the CPO of octane at C/O = 1.0 on Rh-coated foams generates only 6% selectivity on 80 ppi supports and 29% selectivity on 45 ppi catalysts. Also, reactions performed on the same support with the same fuel yield higher selectivities on Pt catalysts than on Rh catalysts. Also, the selectivity of H_2O is fairly constant with respect to the feed C/O ratio.

The selectivity of CO_2 observed from the CPO of normal paraffins is not strongly dependent on fuel molecular weight, support pore size, or catalyst metal and is not shown. In general, the CO_2 selectivity varies between 5 and 15% and increases with decreasing inlet C/O as the stoichiometry approaches that of combustion. For C/O $<$ 1.0, the CO_2 selectivity increases by $<$5% as the reacting fuel chain length increases from methane to hexadecane.

Olefins

Ethylene selectivity is plotted as a function of catalyst metal, support geometry, reacting fuel, and inlet stoichiometry in Figure 6. On 80 ppi Rh and Pt catalysts, the ethylene selectivity increases with increasing molecular weight for alkanes lighter than octane. For example, on 80 ppi Rh catalysts at C/O = 1.2, ethylene selectivity increases from $<$1% for butane, to 3% for hexane, to 15% for hexadecane. The CPOs of octane, decane, and hexadecane produce very similar ethylene selectivities. On 80 ppi Rh catalysts, the maximum ethylene selectivities obtained from reaction with octane, decane, and hexadecane are 20, 21, and 19%, respectively. Similarly, on 80 ppi Pt catalysts, the maximum ethylene selectivity for octane (37%), decane (36%), and hexadecane (38%) are very close even though they occur at different fuel C/O ratios.

The effects of the catalyst metal and support geometry on ethylene selectivity are opposite of their effects on syngas selectivity. On the same support, Pt produces higher ethylene selectivity than Rh. Also, 45 ppi supports prepared without a

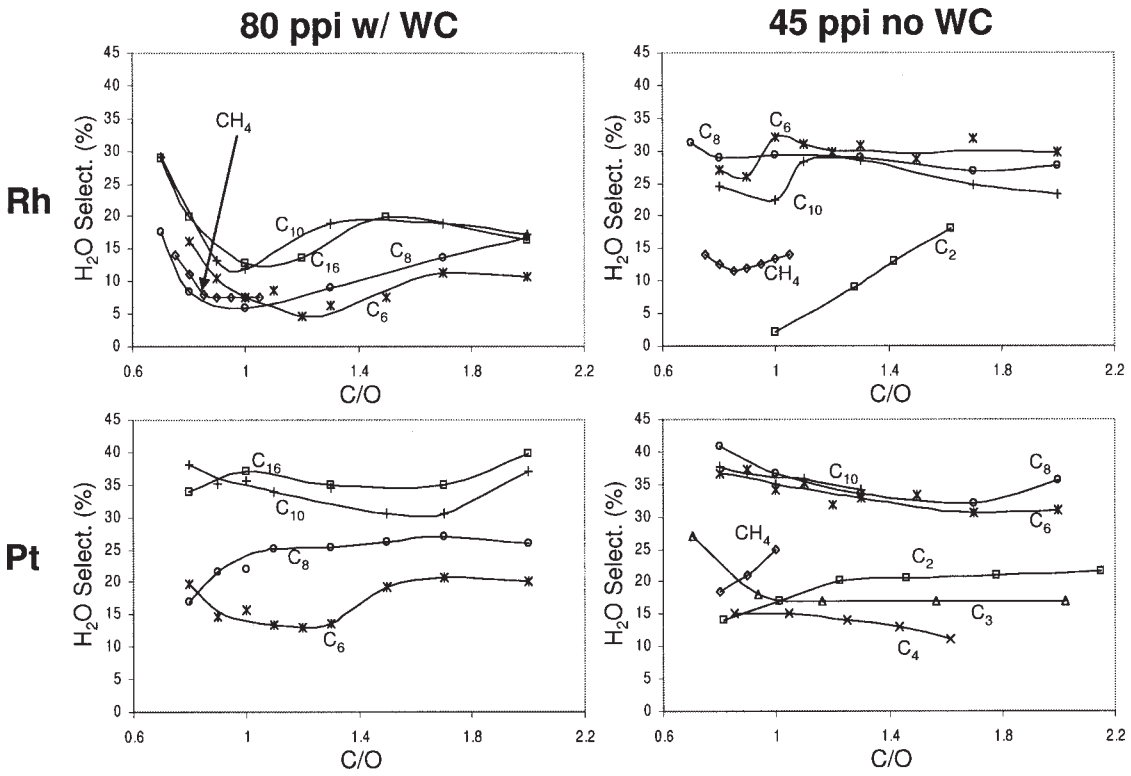

Figure 5. H_2O selectivity for CPO of C_1–C_{16} on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

For the same fuel and catalyst metal, the selectivity of H_2O is greater on 45 ppi with no washcoat supports than on 80 ppi with washcoat supports. Pt catalysts produce more H_2O than Rh catalysts when the same fuel is reacted on the identical supports.

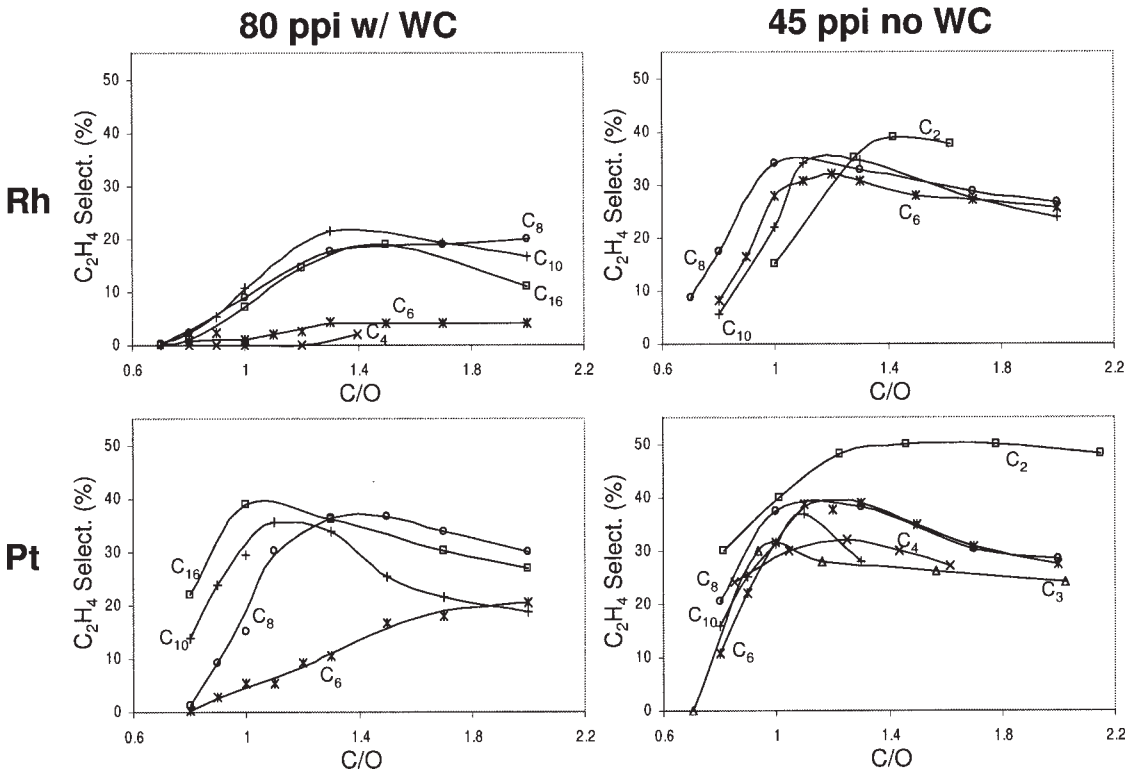

Figure 6. C_2H_4 selectivity for CPO of C_1–C_{16} hydrocarbons on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

On 80 ppi catalysts, C_2H_4 selectivity increases with increasing molecular weight for fuels lighter than octane. Ethylene selectivity is nearly independent of molecular weight for experiments performed on 45 ppi catalysts.

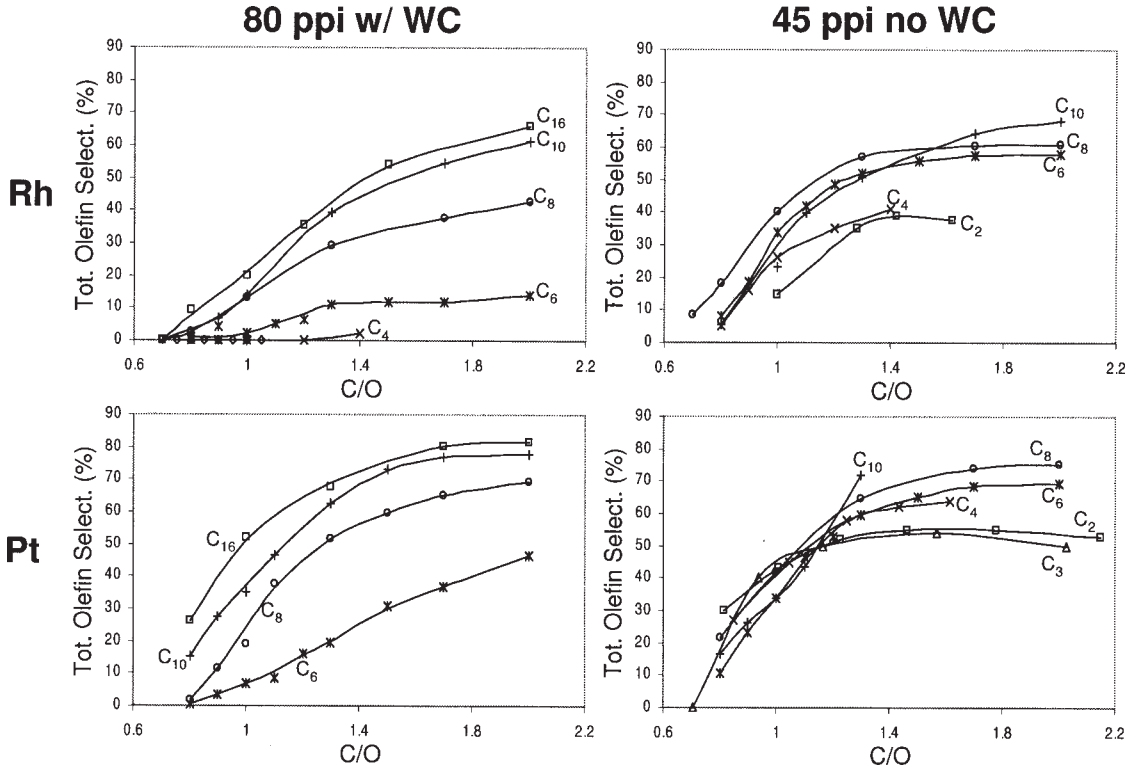

Figure 7. Total olefin selectivity for CPO of C_1–C_{16} hydrocarbons on 80 ppi with washcoat and 45 ppi no washcoat Rh and Pt catalysts.

Total olefin selectivity increases with increasing molecular weight for all catalysts. In general, Pt catalysts produce more olefins than Rh, and 45 ppi no washcoat catalysts have higher olefin selectivities than 80 ppi with washcoat catalysts.

washcoat produce higher selectivity to ethylene than 80 ppi catalysts prepared with a washcoat.

Figure 7 shows the total olefin selectivity as a function of inlet stoichiometry, catalyst metal, support geometry, and reacting fuel. The total olefin selectivity increases with increasing molecular weight on all catalysts, although the effect is more pronounced on the 80 ppi supports that are prepared with a washcoat. For example, on 80 ppi Rh with washcoat catalyst, the maximum total olefin selectivity increases from 2% for butane, to 14% for hexane, to 43% for octane, to 61% for decane, to 66% for hexadecane. This trend continues on 45 ppi no washcoat catalysts, although the difference in total olefin selectivities is not as pronounced.

Discussion

Effect of catalyst support

Previous results on lighter hydrocarbons have shown that catalyst supports with high specific surface areas produce larger amounts of syngas and fewer olefins and water than supports with low specific surface areas.[5] In the current work, the comparison of selectivities obtained from 80 ppi with washcoat catalyst to 45 ppi without washcoat catalyst with the same metal for a single fuel in Figures 3 through 7 shows that this trend also holds for the CPO of heavy alkanes. These results can be explained through a two-zone reaction scheme.

A recent study on the simulation of the CPO of octane isomers and mixtures on Rh-coated ceramic foam monoliths has shown that the CPO system can be accurately described by splitting the reactor into a heterogeneous oxidation zone at the front of the catalyst that is followed by a reforming zone downstream.[10] In the first zone, fuel and oxygen react heterogeneously to form H_2, H_2O, CO, CO_2, and heat. The heat generated in the oxidation zone is used in the reforming zone to homogeneously pyrolyze the remaining fuel into smaller hydrocarbons such as ethylene and other olefins. The ratio of the active surface area to the volume of the gas phase inside the catalytic foam is higher for the 80 ppi catalysts than the 45 ppi foams because the average pore diameter is smaller (0.25 vs. 0.47 mm, respectively) and the surface is roughened by the application of a γ-alumina washcoat. Therefore, the ratio of heterogeneous to homogeneous reactions taking place in the 80 ppi foams should be higher as well. Because H_2 and CO are formed heterogeneously and ethylene and other olefins are formed largely in the gas phase, experiments performed on 80 ppi catalysts should generate higher selectivities of heterogeneously derived syngas, whereas reactions on 45 ppi foams produce greater amounts of homogeneously generated olefins.

The observed experimental selectivity of H_2O also supports the hypothesis that olefins are made through the gas phase by the pyrolysis of heavier hydrocarbons. The selectivities of ethylene and other olefins increase with increasing inlet C/O for all fuels and catalysts (Figures 6 and 7). However, the selectivity of H_2O remains fairly constant with respect to feed C/O over this same range (Figure 5). If olefins

are formed through an oxidative dehydrogenation mechanism,

$$C_xH_{2x+2} + 0.5O_2 \rightarrow C_xH_{2x} + H_2O$$

then the selectivity of water should increase as the olefin selectivities increase. However, if olefins are generated from the pyrolysis of heavier hydrocarbons, then water would not be formed as a coproduct and the selectivity of H_2O would not increase as the selectivity of olefins increases.

Furthermore, the results indicate that the O_2 appears to be consumed before the pyrolysis zone. If O_2 was not consumed upstream of the cracking zone, the H_2 produced from the pyrolysis reactions would likely react with O_2 to produce H_2O at the high operating temperatures. Because the H_2O selectivity remains constant and olefins increase with increasing C/O, the oxidation of the H_2 produced from the pyrolysis of higher hydrocarbons seems not to occur, which supports the speculation that O_2 is absent in the pyrolysis zone.

Difference between Rh and Pt

For the reaction of the same fuel on the same catalyst support, Rh catalysts always generate higher selectivities to syngas and lower water and olefin selectivities than do Pt catalysts (Figures 3 through 7). This suggests that there are consistent mechanistic differences between the heterogeneous reactions taking place on Rh and Pt catalysts for *n*-paraffins ranging from methane to hexadecane. Hickman and Schmidt[21] compared the elementary step surface reaction mechanisms of the direct formation of H_2 from the partial oxidation of methane on Rh and Pt. They found that the primary difference that leads to the large discrepancy in the experimentally measured H_2 selectivities for Pt and Rh lies in the difference in the activation energy for formation of OH on the surface, as in

$$H(s) + O(s) \rightarrow OH(s) + {}^*$$

They found that the activation energy for this reaction on Rh is significantly higher than that on Pt. This energy barrier dictates that less adsorbed hydrogen atoms are going to combine with adsorbed O atoms and are therefore more likely to combine with other H atoms to form H_2 instead of forming water through OH.

It is also possible that the H_2 is formed indirectly. This means that the catalyst promotes the deep oxidation of methane to H_2O and CO_2, which is then catalytically reformed to H_2 and CO through steam reforming and CO_2 reforming overall reactions:

Combustion

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

Steam Reforming

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

CO_2 Reforming

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$

If the indirect formation of H_2 and CO is considered, the discrepancy in the performance of Rh and Pt catalysts with respect to syngas production could be a function of the difference in the activities of the metals. It is possible that both Rh and Pt are efficient oxidation catalysts, but Rh is a much better reforming catalyst than Pt. Leclerc and coworkers recently showed that a dual catalyst bed of Pt followed by Ni can generate similar selectivities to pure Rh catalyst for the CPO of methane.[22] However, a dual-bed catalyst of Ni followed by Pt does not perform as well as the Rh catalyst. In the Pt/Ni arrangement, the Pt catalyst combusts the methane and generates H_2O, CO_2, and heat. The Ni catalyst (which is a very good steam reforming catalyst and is typically used in industrial steam reforming reactors[1]) then reforms the H_2O and CO_2 into H_2 and CO. This supports the hypothesis that both Rh and Pt can function as a combustion catalyst, but that Rh is a better reforming catalyst than Pt.

Effect of fuel chain length

There are several trends that are observed as a function of the chain length (or molecular weight) of the reacting fuel. The results displayed in Figure 2 show that fuel conversion increases with increasing molecular weight for C/O > 1.0. This is probably the result of a combination of two factors. First, the gas-phase reactivity increases for heavier hydrocarbons. This means that, at the same temperature, a heavier fuel is more likely to pyrolyze in the second zone of the catalyst and therefore will have a higher conversion. Also, a previous study on the ignition behavior of *n*-alkanes on Rh during catalytic partial oxidation shows that methane should have a sticking coefficient that is 20 to 40 times smaller than that of *n*-octane.[23] This means that a smaller alkane is much less likely to absorb when it comes in contact with the surface, which also decreases the probability that it will react on the surface compared to a larger hydrocarbon.

The results displayed in Figures 3 and 4 show that syngas selectivity decreases with increasing chain length. Conversely, the total olefin selectivity increases with increasing molecular weight as shown in Figure 7. Both of these phenomena can be explained by the relative reactivity of the reactant fuel in the gas phase. Simulations that combine heterogeneous and homogeneous chemistry to study the CPO of methane at millisecond contact times show that almost no methane is consumed through gas-phase reaction pathways at atmospheric pressure and experimentally observed temperatures.[24] However, other simulations performed for heavier fuels show that a large amount of octane is consumed through gas-phase reaction pathways under these experimental conditions.[10] Given that it has been shown that syngas is formed primarily on the surface and olefins are formed primarily through the gas phase, it follows that the selectivity of the species that are formed in the gas phase should increase relative to the selectivity of the species formed on the surface as the homogeneous reactivity of the fuel increases.

Conclusions

The catalytic partial oxidation of *n*-alkanes ranging from methane to hexadecane has been performed on Pt- and Rh-coated ceramic foam monoliths with different specific surface areas. Catalyst supports with high internal surface area to volume ratios produce high selectivities to syngas, whereas those

with low specific surfaces areas produce high selectivities of olefins. Over the entire range of fuels, Rh is consistently the best catalyst for syngas production, whereas Pt catalysts generate high selectivities to olefins.

Furthermore, trends are observed with respect to the molecular weight of the reacting fuel. As molecular weight increases, fuel conversion and olefin selectivities increase, whereas syngas selectivity decreases—phenomena that arise from the relative reactivity of the fuel in the gas phase. Heavier fuels are more homogeneously reactive and therefore have a higher conversion and produce more olefins than lighter hydrocarbons. Overall, the process is very robust and also very selective. Depending on the application, a system could be designed to generate high yields of either syngas or olefins from a wide range of starting materials.

Acknowledgments

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