Catalytic Partial Oxidation of Higher Hydrocarbons at Millisecond Contact Times: Decane, Hexadecane, and Diesel Fuel

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Introduction

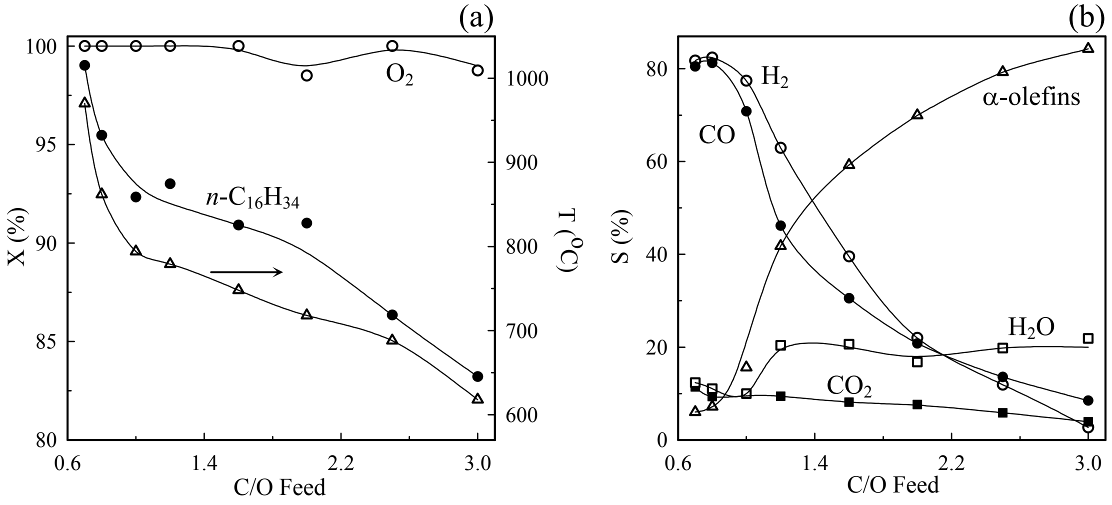
Hydrocarbon reforming is important in many applications to produce fuels such as H_2, and chemical intermediates such as synthesis gas, and olefins. It is accomplished either by steam reforming or steam cracking, which involve reaction with H_2O in endothermic proceses, or by partial oxidation, which involves reaction with O_2 in exothermic processes. While steam reforming and steam cracking of higher alkanes, such as diesel fuel, can be accomplished under suitable conditions, the partial oxidation of higher alkanes presents several problems such as flames during vaporization and mixing, soot formation associated with combustion of fuel-rich gases, and coke formation on reactor walls and on catalysts.

Currently there is considerable interest in reforming logistic fuels such as diesel and JP-8 (military fuel) into light alkanes and especially H_2 for devices such as fuel cells, which function either exclusively on H_2 (the proton exchange membrane fuel cell) or with H_2 in the fuel (the solid oxide fuel cell). There is also considerable interest in fuel reforming for pollution abatement in automotive applications with internal combustion engines. Reforming of gasoline or diesel into H_2 and other small molecules creates a fuel that burns very efficiently, thus reducing or eliminating exhaust emissions of hydrocarbons, CO, and particulate matter. The abatement of NO_x in diesel engines is especially difficult because in a lean burn environment there is insufficient H_2, CO, and small hydrocarbons to react with NO_x in the catalytic converter as there is in the spark ignited gasoline engine. Therefore, reforming part of the fuel and using it to react with NO_x could be important in diesel emissions control.

Here we describe the reforming by partial oxidation of two of the major components of diesel fuel: *n*-decane and *n*-hexadecane, and a low sulfur grade of diesel fuel. We demonstrate the feasibility of these reactions in short contact time reactors using a fuel injector for fuel vaporization and mixing with air.

Results and Discussion

Figure (a) presents the results using hexadecane on a Rh monolith catalyst at 1 atm and 4 SLPM of total flow rate. The catalyst contact time is 6 ms under these conditions. The fuel conversion was > 82% and the oxygen conversion was ~100% at all carbon/oxygen (C/O) ratios. The catalyst back face temperature follows the same trend as the fuel conversion, decreasing as the C/O feed ratio increases. Figure (b) shows that the optimum syngas selectivities of 82% to H_2 and 81% to CO were achieved at C/O = 0.8. As the feed became more fuel rich, the syngas selectivity dropped and the α-olefins selectivity increased. The maximum α-olefin selectivity reached 84% at C/O = 3.



These results show systematic trends with respect to product selectivities as functions of feed composition and fuel type. For all fuels the selectivity goes from mostly CO_2 to CO to small olefins to large olefins as C/O increases. Thus the reactions switch from combustion to reforming to dehydrogenation with increasing C/O,

$$\begin{array}{lcl} \text{Products} & = & CO_2+H_2O \Leftrightarrow CO+H_2 \Leftrightarrow C_2H_4 \Leftrightarrow \alpha\text{-olefins.} \\ \text{Feed C/O} & = & \ll 1 \qquad\qquad \sim 1 \qquad\qquad > 1 \qquad\qquad \sim 2 \end{array}$$

This switch is determined by the amount of oxygen in the feed and the reactor temperature, both of which strongly affect the selectivities.

The conversion generally increases as the molecular weight of the fuel increases. Similarly, the O_2 conversion is higher for higher hydrocarbons. This appears to be qualitatively explained by the higher reactivities of larger hydrocarbons. The C-H bond energy is 104 kcal/mole for CH_4, while the C-C bond energy is 80 kcal/mole for linear alkanes. The selectivities to α-olefins also increase with the molecular weight of the alkane.

These results suggest that only a few dominant reaction pathways operate in these experiments. The detailed chemistry of homogeneous combustion and pyrolysis for these alkanes is well known, but the kinetics of surface reactions have not yet been established. The exact roles of surface and homogeneous reaction steps are unclear in these experiments, but they are probably coupled in this catalyst geometry because of the small channel sizes. By analogy with CH_4[2] and C_2H_6[3] partial oxidation, we suggest that most CO and CO_2 are formed by surface reactions on the Rh surface and that most olefins are formed by homogeneous pyrolysis reactions. We can conclude that the partial oxidation of higher alkanes to syngas and to α-olefins can be successfully accomplished in air.

References

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