268a Catalytic Autoignition of Higher Alkane Partial Oxidation on Rh-Coated Foams

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Catalytic reforming of heavy hydrocarbon fuels (e.g., gasoline, diesel, or jet fuel) to produce a hydrogen-rich reformate has generated great interest for NO_x abatement in diesel engines and electricity production in fuel cells. Transportation fuels are attractive because of their high energy density and widespread distribution infrastructure. To reduce start-up time for mobile fuel processors, it may be favorable to start the fuel processor in catalytic partial oxidation (CPO) mode (exothermic) and then add in water to transition to autothermal reforming mode (thermally neutral).

In this work, the ignition behaviors of higher alkane fuels (i-octane, n-octane, n-decane, and n-hexadecane) on Rh-coated foams were investigated under CPO conditions to better understand the surface processes governing lightoff. In particular, the minimum surface autoignition temperature as well as the ignition delay time as a function of initial surface preheat temperature were determined for each fuel in a near adiabatic reactor. Through online mass spectrometry it is demonstrated that steady-state production of syngas (CO and H_2) can be attained within 5 s after admitting large alkanes (i-octane, n-octane, n-decane, or n-hexadecane) and air into a short-contact-time reactor by using an automotive fuel injector and initially preheating the Rh-coated catalyst above the respective catalytic autoignition temperature for each fuel. Minimum catalytic autoignition temperatures on Rh were ~260°C for n-octane and 240°C for i-octane and n-decane. In contrast, catalytic autoignition of n-hexadecane indirectly occurred at temperatures (> 220^{o}C) lower than those of the other fuels investigated because of exothermic homogeneous chemistry that preheated the catalyst (30-60^{o}C) to a temperature (~280^{o}C) sufficient for surface lightoff.

The ignition kinetics for the large alkanes were also determined and compared with those of methane. The dominant energetic step for large alkane surface ignition is hypothesized to be oxygen desorption at saturation coverage as has been suggested for methane. The step(s) controlling surface ignition possessed an apparent activation energy of ~78 kJ/mol that was not significantly different between fuels ($p > 0.05$). However, a significant difference was found between the ignition preexponential for methane, $O(10^4\ s^{-1})$, and the other large alkanes, $O(10^6\ s^{-1})$. Additionally, the effect of carbon surface coverage on lightoff was examined and found to significantly affect the ignition kinetics.