Fast lightoff of millisecond reactors

C.A. Leclerc*, J.M. Redenius, and L.D. Schmidt

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Received 19 September 2001; accepted 20 November 2001

We show that the partial oxidation of CH_4 to produce H_2 and CO can be accomplished within ~5 s starting at ambient temperature by igniting a stoichiometric feed of CH_4 and air to rapidly heat a Rh on α-alumina catalyst to a temperature where catalytic ignition occurs. By measuring the temperature of the catalyst *versus* time, it is shown that syngas temperatures can be attained within a few seconds, and sampling of product gases shows that H_2 and CO are produced in these times. A simple lumped model of the heating process shows that the high heat generation of combustion and the small mass of the monolith catalyst should be capable of producing these heating rates. This configuration should be useful for fast lightoff in hydrogen generation in transportation and stationary applications of fuel cells for electricity generation.

KEY WORDS: fast lightoff; millisecond reactors; methane; rhodium catalyst; syngas; hydrogen; partial oxidation; combustion.

1. Introduction

Partial oxidation at short contact time has promise for many processes because they can be run autothermally in small reactors. These processes have been used for methane and higher alkanes to CO and H_2 (syngas) [1–5], ethane to ethylene [6,7], and higher alkanes to oxygenates [8]. In the laboratory these processes can produce several kilograms per day of product from less than 1 g of catalyst with contact times on the catalyst from 0.1 to 10 ms. In H_2 generation for a fuel cell these experimental conditions could produce ~1 kW of electricity.

We and others [1–5] have typically started these reactors by preheating the gases or the catalyst with heating tape, in an oven, with an external flame, or by electrical heating of the catalyst. These processes require times of minutes for lightoff, after which the process is autothermal with no external process heat required.

These processes have large scale industrial applications, for example in methane to syngas for ammonia, methanol, or synthetic diesel fuel. In these applications the process would operate for long times at nearly steady state, so long startup procedures are not a major problem.

However, H_2 and CO have other uses in small systems for fuel cells in transportation [9] and stationary applications. For these systems, fast lightoff and rapid response to transient load demands are crucial, so long lightoff times are unacceptable.

In this paper we show that millisecond reactors can be ignited and produce high selectivities to H_2 and CO from room temperature in less than 5 s. We accomplish this by internal heating of the catalyst using combustion to produce CO_2 and H_2O

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad \Delta H = -800\,\mathrm{kJ/mole}. \tag{1}$$

Near the stoichiometric ratio for this reaction (defined as $\phi = 1$) the adiabatic temperature is >2000 °C, so any catalyst would rapidly be destroyed under these conditions in steady state. However, by rapidly switching from the combustion ratio to the syngas ratio ($\phi = 4$), the reaction

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \qquad \Delta H = -36\,\mathrm{kJ/mole} \tag{2}$$

produces a steady state temperature of ~900 °C.

We examine conditions for optimum lightoff of this reaction in a laboratory reactor that produces ~5 kg/day of syngas. We determine the temperature *versus* time and estimate product selectivities *versus* time to test the feasibility of this system. The primary issue we address is the transient response of the system in temperature and selectivity. The ability of the catalyst system to withstand the large thermal gradients that could limit the operation of the system, and the time required to switch from combustion to syngas products could limit its usefulness.

Ignition of wire catalysts in combustion and partial oxidation of CH_4 and other alkanes have been examined in detail [10,11]. It was shown that metals such as Rh can be ignited catalytically at atmospheric pressure by electrically heating the wires to ~300 °C. In this paper we use combustion heating of Rh catalysts supported on alumina foams.

---

* To whom correspondence should be addressed.

1011-372X/02/0400-0039/0 © 2002 Plenum Publishing Corporation

2. Experimental

The reactor was similar to those described previously for millisecond autothermal processes. Basically it consisted of an 18 mm diameter quartz tube containing an α-alumina foam disc ~10 mm long impregnated with Rh which catalyzes formation of syngas with ~90% conversion at ~90% selectivities to H_2 and CO.

As sketched in figure 1, the system was modified slightly for fast lightoff. The catalyst was preceded by an uncoated 45 ppi (pores per linear inch) α-alumina foam which acted as a gas mixer and flame stabilizer. After this foam, an empty ignition compartment ~1 cm long preceded the catalyst which was 80 ppi α-alumina coated with ~5% Rh by weight as described previously [12]. Following the catalyst was another uncoated α-alumina foam that acted as a radiation shield.

Electrodes to generate a spark in the ignition compartment were powered by a piezoelectric device. Shielded thermocouples measured the temperatures in the ignition compartment and on the back face of the catalyst. The entire assembly was insulated with glass wool to nearly adiabatic operation.

In operation, gas flows of CH_4 and air were first established at 25 °C near $\phi = 1$. Then the spark ignited the mixture in the ignition compartment which produced a visible blue glow. Then after 2 to 10 s the CH_4 flow was turned up to $\phi = 4$, the syngas ratio.

The system was controlled and temperatures measured using a programmable logic controller which automatically switched the CH_4 flow rate at a specified time after spark ignition. We regard times quoted as accurate to within ±1 s.

An on-line gas chromatograph was used to measure steady-state gas compositions, verifying high yields of syngas as expected. To determine product gas compositions during lightoff, we used a gas sampling syringe inserted in a sidearm in the reactor ~12 cm downstream from the catalyst. Approximately 2 s were required to fill the syringe, so these times are only accurate to within that interval. The reactor had to be restarted for each syringe measurement, and a continuous mass spectrometer sampling system is being assembled for more accurate transient gas analysis.

We repeated most experiments on several catalysts. However, the catalysts were quite stable, and a single catalyst was used for ~50 lightoff sequences in which the temperature of the catalyst was repeatedly and rapidly cycled from 20 °C to ~900 °C. While overheating above 1100 °C deactivated the catalyst by evaporation of Rh, no deactivation or degradation of the catalyst was observed in normal operation over many cycles.

For all experiments shown here we used a slightly lean mixture at $\phi = 0.95$ for ignition and the syngas stoichiometry of $\phi = 4$ ($CH_4/O_2 = 2.0$) for syngas generation. This assured nearly complete combustion of CH_4 during ignition. For syngas generation, higher yields would be obtained at $\phi = 3.6$ [4–6], but we used 4.0 for these experiments.

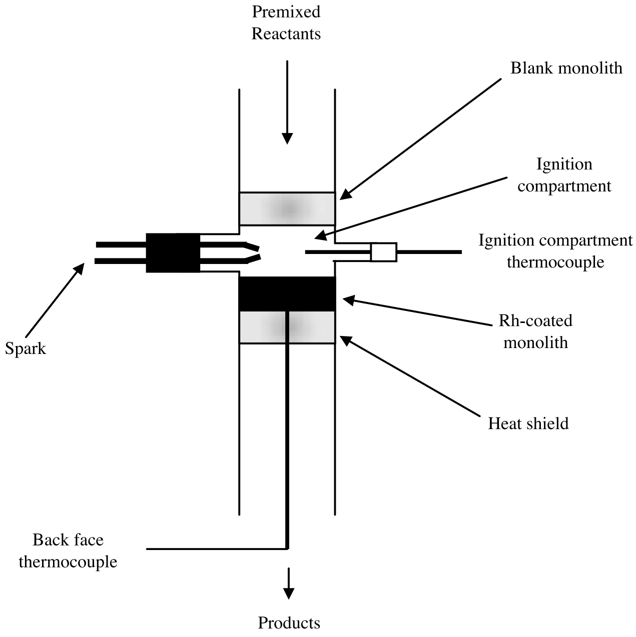

Figure 1. Reactor configuration. A spark in the ignition compartment with gases flowing at the combustion ratio rapidly heats the catalyst (black) to the ignition temperature, after which the gases are switched to the syngas composition.

3. Results

We measured the effects of switching time, gas flow rate, catalyst thickness, combustion composition, ignition compartment length, and reactor orientation on performance.

3.1. Switching time

In these experiments an air flow of 5 l/min was used for total flows of 5.5 and 7.0 l/min in combustion and in syngas generation respectively. Figure 2 shows thermocouple temperatures (a) in the ignition compartment and (b) on the back face of the catalyst for switching times of 2, 6, 9, 10, and 12 s. Each was a separate experiment, but the curves during combustion before switching are nearly identical, as expected. We estimate the accuracy of switching times as ~1 s.

The ignition compartment thermocouple reading is lower than the actual gas temperature in the compartment which we assume to rise to nearly its maximum value in much less than 1 s. Upon switching, the flame extinguishes, and the recorded temperature decreases, but it does not reach ambient temperature because of radiation heating of the compartment walls from the hot catalyst.

Even for switching after 2 s, the catalyst ignites, but ~10 s is required to approach steady-state temperature.

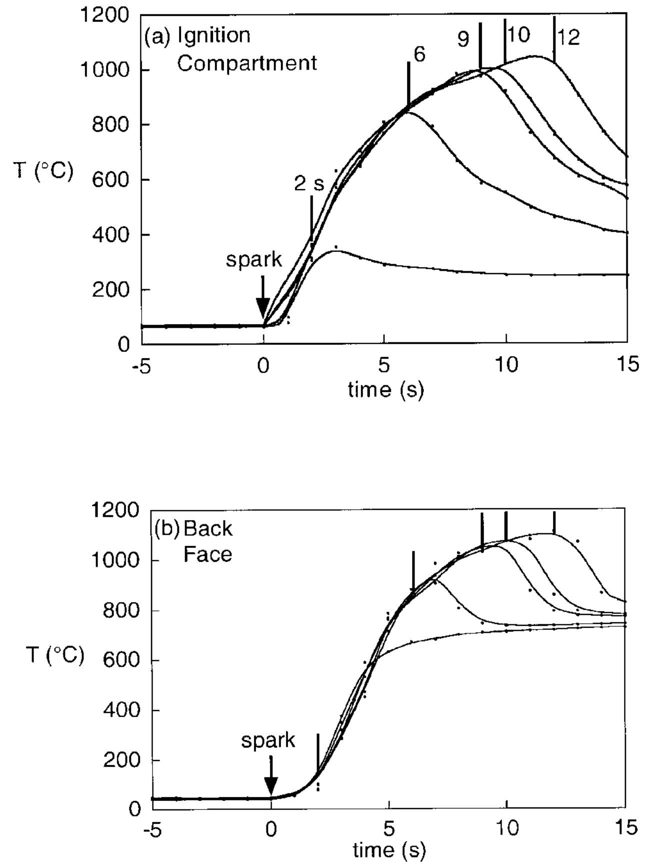

Figure 2. Effects of switching time with a constant air flow rate of 5 SLPM and 5 mm thick catalyst for (a) ignition compartment temperature and (b) back face temperature. A spark ignited a combustion mixture at $t = 0$ and the CH_4 flow rate was increased to the syngas ratio ($\phi = 4$) at the time shown.

The conduction of heat from the 1000 °C front face of the catalyst to the back face and heat generated from syngas production on the front of the catalyst account for the continued heating of the back face. For switching at times longer than 6 s, overshoot in the back face temperature is evident.

3.2. Flow rate

We examined the effect of gas flow rate by using air flow rates of 2.5, 5.0, 7.5, and 9 l/min, holding compositions before and after switching constant. As shown in figure 3 for switching after 4 s, the heating rates are strongly dependent on flow rate. The final temperatures also depend on flow rate, increasing initially with flow rate but reaching a constant temperature which is presumably near the adiabatic temperature, as expected.

At lower flow rates the rate of heating is proportional to flow rate but, between 7.5 and 9 l/min of air, there is little change in heating rate. We believe this is because at high flow rates the flame begins to impinge on the catalyst surface, thus producing incomplete combustion.

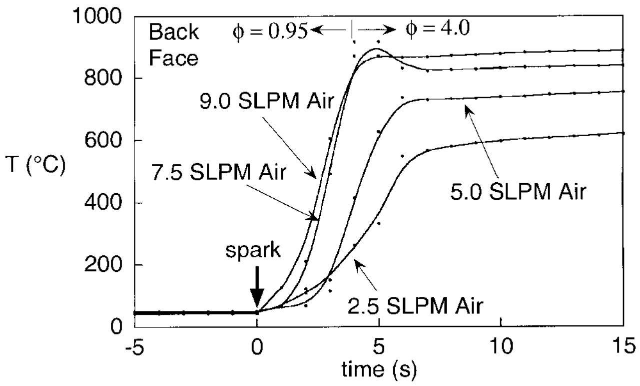

Figure 3. Effects of flow rate on back face temperature of a 5 mm thick catalyst with a switch time of 4 s. Higher flow rates produce higher heating rates because of higher heat generation rates.

3.3. Catalyst thickness

We used catalyst foams of 3, 5, and 10 mm length, each loaded with 5% Rh, to determine how the heating rate depended on the mass of the catalyst. Figure 4 shows these results for an air flow rate of 5 l/min and a switching time of 7 s. It is seen that the 3 mm catalyst heats fastest and its temperature is nearly 1000 °C in 7 s. The 10 mm long catalyst heats the slowest and exhibits a lag in that the back face temperature does not begin to rise until ~5 s after ignition.

3.4. Estimation of selectivities and conversion during lightoff

We estimated selectivities and conversions during lightoff using gas chromatography by gas sampling with a syringe. These results are shown in figure 5. It is seen that the CO selectivity is ~90% within a few seconds of switching and that the H_2 selectivity rises to nearly its steady state within ~10 s. We emphasize that times and selectivities may be rather inaccurate because of sampling errors. However, these results clearly show that significant H_2 and CO are produced immediately.

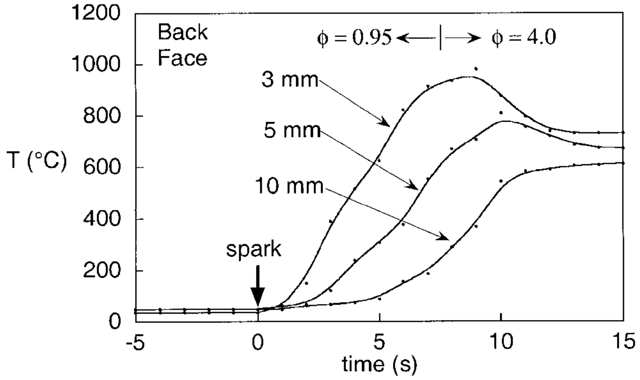

Figure 4. Effects of catalyst thickness with a constant air flow rate of 5 SLPM and switching to the syngas ratio after 7 s. Shorter thicknesses produce more rapid heating, because of smaller mass.

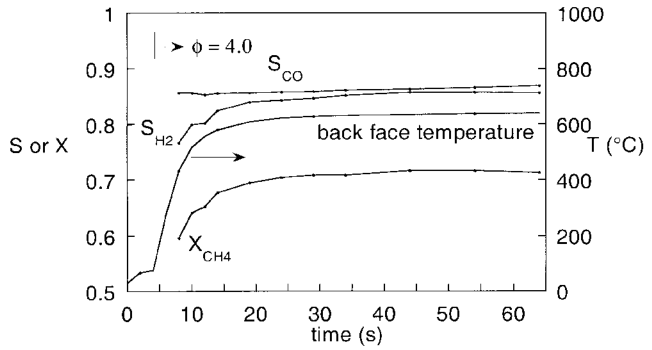

Figure 5. Temperature, CH_4 conversion and H_2 and CO selectivities in startup on a 1 cm thick catalyst at 5 SLPM of air switched to syngas at 4 s, measured by gas chromatography, sampled with a syringe at the time shown. The reactants were switched from combustion composition ($\phi = 1$) to the syngas composition ($\phi = 4$) at 5 s. The CO selectivity attains steady state within 3 s, but the temperature, CH_4 conversion and H_2 selectivity required ~10 s to approach steady state.

The CO appears to rise to nearly its steady state within a few seconds after switching, while the CH_4 conversion and H_2 selectivity attain steady state in ~5 s.

The variation of the steady state conversion and selectivity with flow rate is shown in figure 6. These results were obtained with on-line gas chromatography several minutes after lightoff. These results show that between 2.5 and 9 l/min the conversion and selectivities are nearly constant, although at the highest flow rate the conversion and selectivities begin to decrease. This indicates that this reactor should be able to operate over a wide range of flow rates with little deterioration in performance. The lower limit is determined by lower temperatures because heat generation is too low, and the upper limit is determined by blowout.

3.5. *Composition, compartment length, and reactor orientation*

We also measured the effects of these parameters, although the variations were small and are not shown here. We varied the ignition stoichiometry between $\phi = 0.9$ and 1.1. We observed little variation in ignition characteristics except that the heating rate was lower away from $\phi = 1$ as expected. Below $\phi = 0.9$ it was difficult to ignite the flame.

The ignition characteristics were nearly the same when the length of the ignition compartment was varied from 3 mm to 2 cm. As noted above, a longer ignition compartment should permit operation at higher flow rates to permit the flame to be complete before entering the catalyst section. Performance was also nearly identical for flow up, flow down, and horizontal orientations. We noted slight variations that changed as expected for heat storage due to the downflow of hot gases.

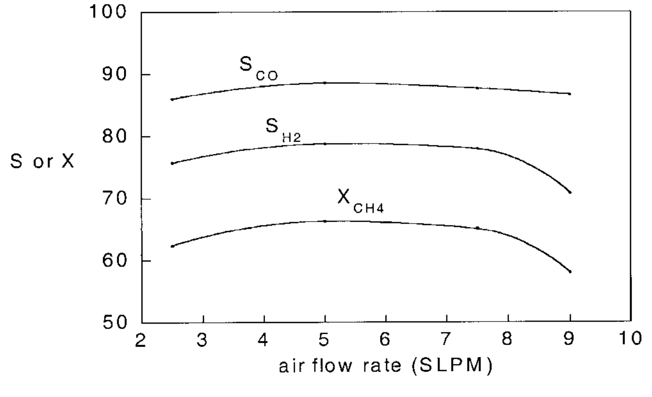

Figure 6. Effects of flow rate on steady state syngas yields of a 5 mm thick catalyst. Results shown are for lightoff experiments of figure 4 for times ~5 min after lightoff. Selectivities and conversions are nearly independent of flow rate, but decrease at 9 SLPM.

4. Discussion

4.1. *Transient Response*

These experiments show that syngas can be produced within ~5 s after igniting the system from room temperature by combustion heating. They also show that syngas can be obtained within a few seconds after switching from the combustion stoichiometry to the syngas stoichiometry.

It should be noted that the temperature of the catalyst is a function of both time and position, $T(z, t)$, in transient experiments. The temperatures in the figures are measured at the back face of the catalyst foam. This is the lowest temperature initially because the front of the catalyst is heated first. However, after switching to the syngas composition, the front face should cool first, so the temperature profile could be inverted. Finally, in steady state, the front face should be at the highest temperature because most heat is generated there. Any consideration of conversions and selectivities must include the effects of temperature profiles in the transient situation.

The steady-state selectivity to syngas depends strongly on the temperature of the catalyst as well as on the fuel/oxygen ratio, as shown by experiments [13] and by detailed modeling of the process [14]. At the syngas composition, CO is the dominant product over a wide range of temperatures, but H_2O dominates over H_2 if the temperature is below ~800 °C [15]. This temperature dependence is confirmed in these transient experiments, as shown in figure 5. Thus, the observed transients in CO and H_2 appear to be explainable qualitatively from the temperature variation within the catalyst in transient operation. However, there may be some transient in products formed caused by Rh surface coverage transients in the heating process. Separation of temperature effects from coverage effects will require more detailed experimental measurements of composition *versus* time as well as more detailed simulation of predicted coverage variations in transient operation.

4.2. Simulation

A simple lumped model of this system explains most results qualitatively. We consider a catalyst of mass M and specific heat C_p which is heated at a rate Q. Heat losses from this system are $UA(T - T_0)$, where U is the heat transfer coefficient, A the heat transfer area, and T_0 the ambient temperature. This gives a transient equation

$$MC_p \, dT/dt = Q - UA(T - T_0).$$

For this monolith catalyst the mass of the catalyst is 2.1 g and the specific heat of alumina is 1.2 J/g K. At a flow rate of 1.67 l/min at the combustion stoichiometry the rate of heat generation is $Q = 1000\,\text{W}$. This predicts $dT/dt = 400\,\text{K/s}$, so the time required to increase the temperature by 400 K is 1 s.

Thus the heating rate and heating time observed are consistent with this simple heat flow calculation. The actual curve of $T(t)$ is calculated by integrating the above equation. If Q, M, and C_p are constant this yields

$$T(t) = T_0 + Q/UA\{1 - \exp[-(UA/MC_p)t]\}. \quad (3)$$

Solutions of this equation for parameters in figure 2 are plotted in figure 7(a). It is seen that agreement is quite good considering that there are no adjustable parameters except UA.

This simple model also predicts the dependence on flow rate and catalyst thickness. Figure 7(b) and (c) shows plots of predicted temperature of the catalyst *versus* time for these experiments, and all trends are in good qualitative agreement. The flow rate determines Q and the catalyst thickness determines M, so again there are no adjustable parameters. After the switch time the heating rate Q was changed to correspond with the heat production during partial oxidation. Since partial oxidation is not as exothermic as combustion, *i.e.* Q decreases, it cannot maintain the same high temperatures and the temperatures fall.

A major deficiency of the model is that it assumes that the temperature is independent of position, whereas in the heating experiment the front face of the catalyst is obviously hotter than the back face where temperature is measured. This accounts for the time lag when ignition is begun. A more detailed model which calculates $T(z, t)$ would predict the lag time in back face temperature increases, and we have begun these simulations. However, we note here that this lumped model, which assumes infinite heat conduction within the catalyst to maintain its temperature uniform, predicts experimental behavior remarkably well.

Also excluded in this model is the kinetics. While in the ignition time interval the reactants are probably consumed to produce CO_2 and H_2O before the gases enter the catalyst, the actual prediction of behavior during syngas production requires use of detailed kinetics. This in turn requires solution of the partial differential equations during the heating transient. These calculations are in progress.

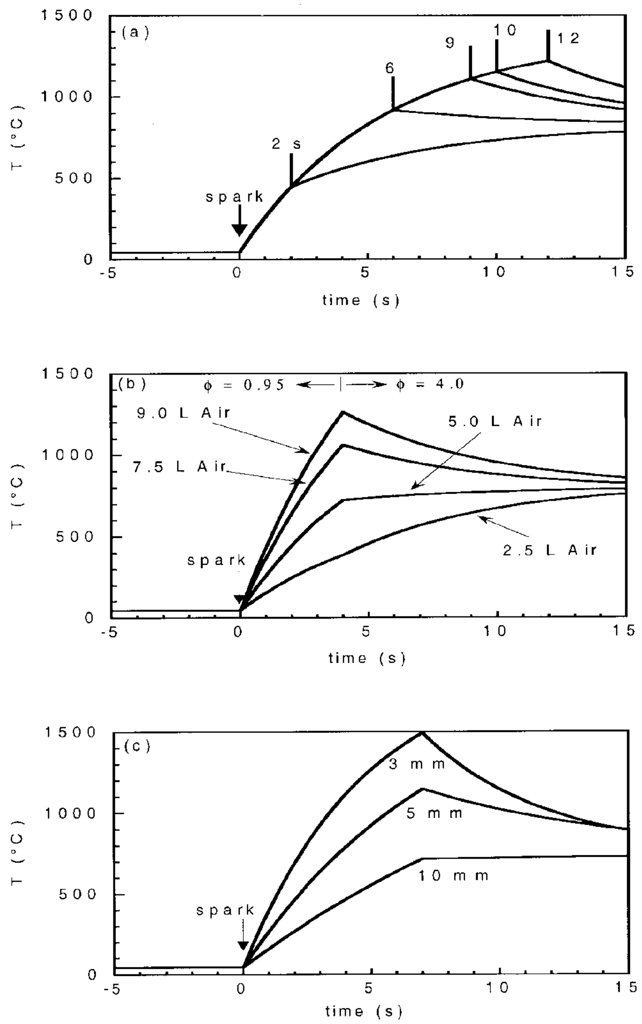

Figure 7. Simulation results for (a) switch time for experiments of figure 2, (b) flow rate from figure 3 and (c) catalyst thickness from figure 4. These calculations are for the lumped model of equation (3) with experimental parameters in the figures.

5. Summary

Lightoff of millisecond reactors can be accomplished in a few seconds starting from room temperature. Initiation with homogeneous combustion heats the catalyst very rapidly because of the very high heat of combustion compared with the heat released in partial oxidation. The other factor in generating rapid temperature rise is the small heat capacity of the monolith reactor.

These experiments demonstrate that approximately 1 kW of energy in the form of H_2 and CO (assumed combusted to CO_2 and H_2O in a fuel cell) can be produced in a 1 cm^3 catalyst system that can be ignited in a few seconds starting from room temperature. These experiments also show that the rate of heating can be increased by using high gas flow rates and small mass of catalyst. The limits to these parameters are obviously the flow where the flame cannot be sustained and the mass where reaction is incomplete. Various engineering considerations can be used to extend these limits to even higher production rates for small reactor systems.

The use of combustion for ignition also reduces or eliminates pollution from unburned hydrocarbons, CO, and NO_x in this time because ignition is at the stoichiometric composition or slightly lean. Therefore there should be little of these gases produced during lightoff. Replacing this homogeneous combustion system with a catalytic combustor operating with a leaner fuel mixture would further reduce these pollutants during ignition. Operation of this reactor with higher hydrocarbons such as propane should be possible, and gasoline should be possible if vaporization can be accomplished efficiently.

Acknowledgment

This research was partially sponsored by Delphi Automotive and the National Science Foundation.

References

[1] L. Basini, A. Guarinoni and A. Aragno, J. Catal. 190 (2000) 284.
[2] Y. Ji, W. Li, H. Xu and Y. Chen, Catal. Lett. 71 (2001) 45.
[3] W. Yanhui and W. Diyong, Int. J. Hyd. Energy 26 (2001) 795.
[4] R.P. O'Connor, E.J. Klein and L.D. Schmidt, Catal. Lett. 70 (2000) 99.
[5] S.S. Bharadwaj and L.D. Schmidt, Fuel Proc. Tech. 42 (1995) 109.
[6] L.D. Schmidt and M. Huff, Catal. Today 21 (1994) 443.
[7] P.M. Witt and L.D. Schmidt, J. Catal. 163 (1996) 465.
[8] R. O'Connor and L. Schmidt, Chem. Eng. Sci. 55 (2000) 5693.
[9] J.E. Kirwan, A.A. Quader and M. J. Grieve, SAE Paper 012927 (1999).
[10] G. Veser, M. Ziauddin and L.D. Schmidt, Catal. Today 47 (1999) 219.
[11] M. Ziauddin, G. Veser and L.D. Schmidt, Catal. Lett. 46 (1997) 159.
[12] A. Bodke, S. Bharadway and L.D. Schmidt, J. Catal. 179 (1998) 138.
[13] D.A. Hickman, E.A. Haupfear and L.D. Schmidt, Catal. Lett. 17 (1993) 223.
[14] D.A. Hickman and L.D. Schmidt, AIChE J. 39 (1993) 1164.
[15] D.A. Hickman and L.D. Schmidt, Science 259 (1993) 343.