Catalytic Incineration of VOC Containing Air Streams at Very Short Contact Times

C. T. Goralski, Jr., and L. D. Schmidt
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

W. L. Brown
Rust Environment & Infrastructure, Minneapolis, MN 55441

A short-contact-time catalytic combustor described here is capable of incinerating air streams with low concentrations of volatile organic compounds (VOCs) at conversions exceeding 99.5% for contact times on the order of 5 ms. This is accomplished by adding methane to the VOC-containing air stream to increase the fuel stream value and then passing the mixture over a platinum-coated foam ceramic monolith at 900–1,400°C. The incineration of air streams containing toluene, chlorobenzene, acetonitrile, and thiophene was examined at concentrations ranging from 500 to 2,000 PPM. Residence time and methane concentration do not affect strongly the outlet concentration of the VOC and conversion. Greater than 99.5% conversion is observed for all compounds examined for residence times ranging from 4 to 12 ms and methane concentrations from 5.5 to 7.0% (80–40% excess air). The mechanism of reaction in this system is primarily heterogeneous, with some homogeneous reactions driven by the heat liberated by the heterogeneous reactions. A simple homogeneous model shows that homogeneous chemistry alone cannot account for complete conversion of the additional methane fuel at the reaction conditions described.

Introduction

Short-contact-time catalytic reactors have shown great promise to produce partial oxidation products at very high selectivities and conversions to desirable products. Examples of these systems are the production of syngas from methane described by Hickman (1992, 1993), the conversion of ethane to ethylene described by Huff and Schmidt (1993), and the conversion of cyclohexane to olefins described by Dietz (1997). All of these systems pass fuel-rich gas streams over noble-metal monoliths at relatively high temperatures to produce partial oxidation products. We have previously described work where similar reactors were operated in the fuel-lean regime to combust methane, ethane, propane, and butane at very high conversion (> 99.5%) to produce complete oxidation products of carbon dioxide and water (Goralski and Schmidt, 1996). In this article we carry this work further by adding volatile organic compounds to the inlet of this reactor using methane as a fuel to investigate the use of this system as a short-contact-time catalytic incinerator.

Tightening regulations of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) emissions will bring new challenges for both large and small industry to reduce the amount of these pollutants released into the atmosphere (Shirley, 1994). One particularly difficult problem is the abatement of point-source emissions that have a relatively low VOC concentration and hence a low fuel value. Examples include exhaust from paint booths and curing ovens, drying of inks at printing operations, and the drying of pulp or paper products. Current control technologies for these types of process emissions include catalytic and thermal incineration to convert the pollutant to carbon dioxide (CO_2) and water (H_2O), or adsorption to capture and recycle the pollutant. The majority of control technologies currently in use utilize relatively large and expensive equipment that can be costly to operate and maintain. In this article we demonstrate a new short-contact-time catalytic incinerator that will completely oxidize VOCs at greater than 99.5% conversion using equipment up to 250 times smaller than the oxidation systems currently available. In addition to being smaller than

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Correspondence concerning this article should be addressed to L. D. Schmidt.

current combustors, this catalytic reactor eliminates other problems associated with other types of incinerators, such as catalyst poisoning and potential production of oxides of nitrogen (NO*x*) (Clarke and Williams, 1991).

Conventional catalytic incineration

Catalytic incineration is becoming an increasingly popular method for the abatement of VOCs from process exhaust streams. A typical catalytic incineration system is shown in Figure 1a (Chu, 1994). The VOC-contaminated inlet gases are preheated in a heat exchanger using the sensible heat of the exhaust gases. Additional heat is often provided in the preheating zone, which acts much like a gas furnace. These incinerators typically operate with bed inlet temperatures of ~ 300°C and outlet temperatures of ~ 650°C. The heated inlet gases then pass through the catalyst bed and react to form carbon dioxide and water. The catalyst bed consists either of a high surface area extruded ceramic monolith or porous alumina spheres supporting a highly dispersed platinum group metal catalyst (Heck and Farrauto, 1995). These incinerators typically exhibit destruction efficiencies of 95% at residence times on the order of 0.1 s and 99% at residence times on the order of 1 s (Chu and Windawi, 1996).

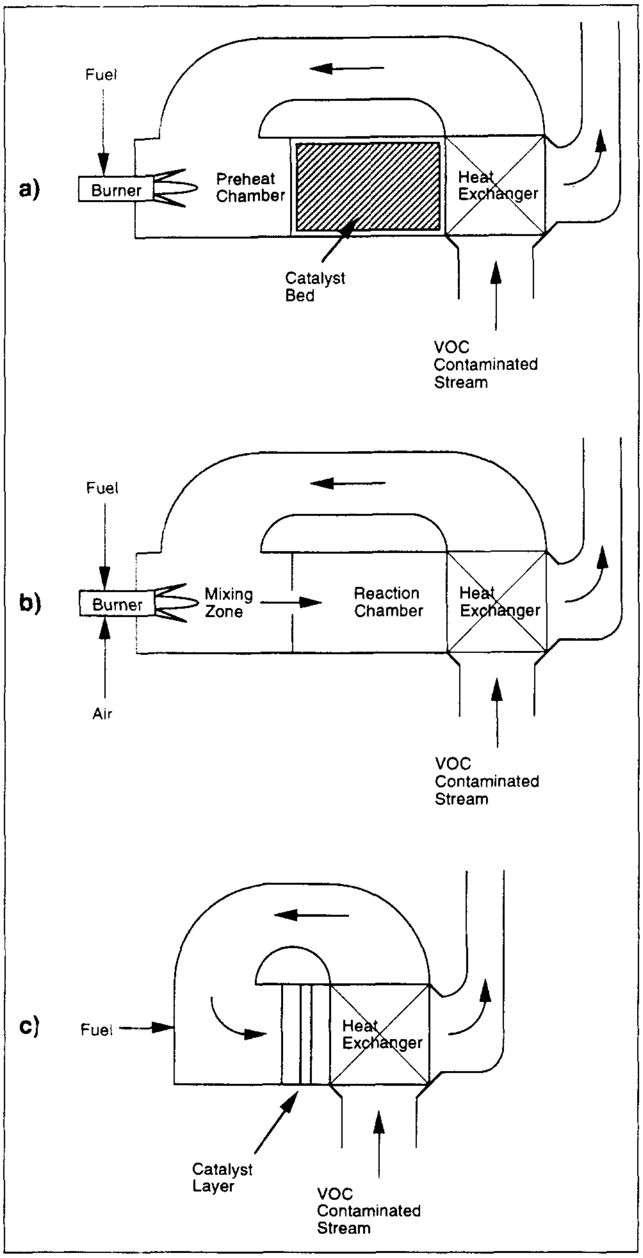

Figure 1. (a) Typical catalytic incinerator; (b) typical thermal incinerator; (c) short-contact-time catalytic incinerator.

The most common problem seen in catalytic incinerators is catalyst deactivation from either thermal or chemical degradation. Thermal degradation is observed when the catalyst is exposed to high temperatures (> 700°C), where sintering of the catalyst particles and the washcoat can occur. This type of degradation is irreversible and results in a loss of both surface area and active catalyst sites, leading to a loss in overall catalyst activity (Chu and Windawi, 1996).

Chemical deactivation, or poisoning, of a catalyst occurs when a compound is adsorbed irreversibly onto an active site on the catalyst and renders the site inactive. The most common poisons present in catalytic incineration systems are heavy and base metals, silicon, and sulfur- or chlorine-containing compounds (Spivey, 1987). These poisons are strongly adsorbed on the active sites of the catalyst at the relatively cool bed temperatures, causing deactivation of the catalyst. Deactivation can also occur because of the buildup of high-molecular-weight organic material such as coke and soot (Heck and Farranto, 1995).

Thermal incineration

Thermal incineration is probably the most common technology used to control VOC emissions from point sources. Figure 1b shows a thermal incinerator (Chu, 1994). The main components of a thermal incinerator system are the reaction chamber and the heat exchanger. Gases from the emission source are passed through a heat-exchanger system and are preheated by the exhaust gases from the combustion chamber. The inlet gases then enter the combustion chamber where they react to form carbon dioxide and water. Typically, dilution air can be added to the gas mixture before the preheater if the stream is too rich in fuel. There is also a supplementary fuel line fed to the combustor to increase the fuel value of the gas mixture if needed. The supplementary fuel is typically natural gas or liquefied petroleum gas (LPG). The fuel is ignited in the preheating zone as a diffusion flame to increase the temperature of the inlet stream (Buonicore and Davis, 1992). It is this process that leads to high peak temperatures and potential problems with the emissions of NO*x*.

Conversions of 99% can be achieved in thermal incinerators at temperatures of ~1,000°C at residence times of 0.75 s for nonhalogenated process exhaust streams. Process exhaust streams containing halogenated compounds typically require residence times on the order of 1 s at temperatures of ~1,200°C for 99% conversion (Patkar and Laznow, 1992).

Short-contact catalytic incineration

The reactor used in the experiments described here differs considerably from the two types of reactors described previously. The short-contact-time catalytic reactor consists of a low surface area (< 1 m^2/g), nonporous supported noble-metal catalyst placed in a tubular reactor. By using a low-surface-area catalyst, much higher catalyst temperatures (> 1,000°C) can be achieved without loss of surface area and activity caused by sintering of the catalyst as is often seen in high-surface-area supports. This is because the noble metal is present as a thin film coating the surface of the catalyst, rather than highly disperse crystallites; therefore, any sintering or relocation of the metal would result in a gain in surface area. In addition, higher surface temperatures make this catalyst more resistant to catalyst poisons such as sulfur, nitrogen, and chlorine than typical combustors because these poisons will rapidly evaporate from the catalyst surface at the elevated temperatures in the short-contact-time catalytic reactor. By using a catalyst, however, we can operate the reactor at cooler peak temperatures than those typically seen in homogeneous combustors (> 1,500°C), and thus almost eliminate the potential for the production of NO_x.

By using this type of reactor, we have been able to achieve conversion exceeding 99.5% for air streams containing 500–2,000 ppm of toluene, chlorobenzene, acetonitrile, and thiophene for contact times ranging from 4 ms to 12 ms at catalyst temperatures between 900 and 1,400°C. This represents a reduction in residence time of approximately 250× when compared to either thermal or conventional catalytic incineration.

Experimental Studies

The experimental apparatus consisted of a quartz tube reactor with a platinum- or palladium-coated foam monolith catalyst placed in the reactor. Mass-flow controllers were used to control the flow rate of gases to the reactor, and a liquid vaporization system was used to create an air stream containing VOCs. Gas chromatography was used to measure the amount of unreacted VOCs in the product streams. Figure 2 shows a diagram of the apparatus.

The reactor used was a quartz tube reactor 18 mm in diameter. A 45 pore-per-inch (ppi) α-alumina foam monolith (custom-made by High Tech Ceramics) 17 mm in diameter and 10 mm thick was coated with ~5 wt. % platinum or palladium and used as the catalyst. The catalyst was wrapped in alumina cloth insulation (Fiberfrax 880f, available from Unifrax, Inc.) and placed in the reactor. The catalyst was prepared in the same manner as previously published (Huff et al., 1994). The cloth insulation acted both to prevent heat loss in the radial direction, as well as to prevent unreacted gases from bypassing the catalyst. Heat shields made of 45-ppi α-alumina monoliths with the same dimensions as the catalyst were placed directly up- and downstream of the catalyst to prevent heat loss from the catalyst by radiation. The temperature of the catalyst was measured by placing a Pt-Pt/13% Rh thermocouple on the downstream face of the catalyst.

Nitrogen, oxygen, and methane were supplied to the reactor using mass-flow controllers with an accuracy of ±5%. Simulated VOC-containing streams were created by bubbling air through a two-stage evaporator, as shown in Figure 2, to create a gas stream saturated with the liquid solvent upon exiting the evaporator. The temperature of the evaporator was regulated by placing the evaporation chambers in a well-stirred constant-temperature water bath. Saturation was ensured by varying the air flow rate to the evaporator and checking to ensure that the concentration of vapor in the air at the exhaust of the evaporator remained constant over the flow-rate range of interest. The saturated VOC/air stream was then mixed with the nitrogen, oxygen, and methane streams and fed to the reactor. The resulting mixtures were in the fuel-lean composition regime (< 9.5% methane) for all cases reported here.

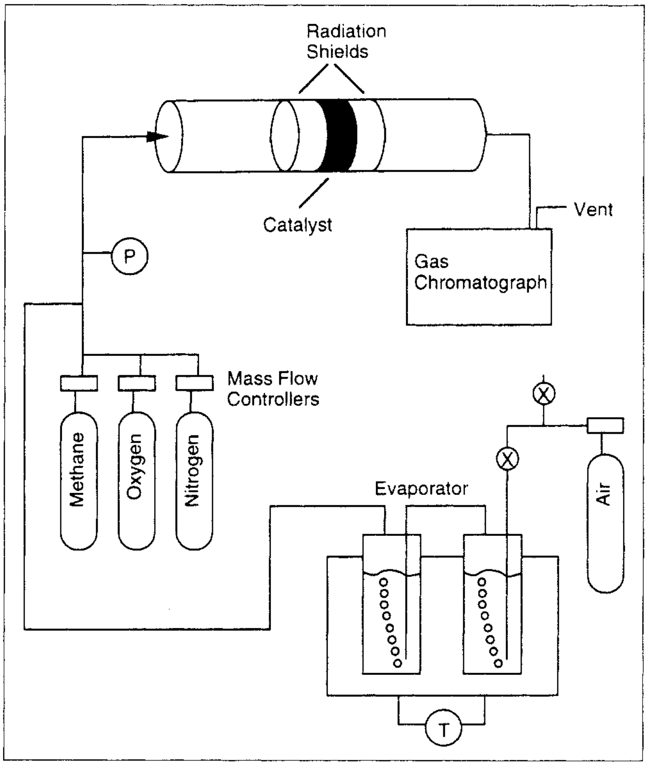

Figure 2. Experimental apparatus.

All experiments were run with the inlet gases at ambient conditions (no preheat). The catalyst was ignited by holding a Bunsen burner flame next to the catalyst in the quartz tube until the catalyst was visibly ignited. The reaction zone was then insulated with alumina fiber insulation and aluminum foil, and the reactor operated autothermally.

The composition of the exhaust gases from the reactor were measured using a gas chromatograph equipped with a thermal conductivity detector and a flame ionization detector and were then exhausted into a fume hood. Stainless-steel packed columns were used for all cases. The column packings used were Chemipack C18 to achieve separation of heavier components and Hayesep D for light components.

Gas injections were performed both manually with a syringe and by direct injection of the exhaust gas from the reactor piped to the gas chromatograph using a pneumatic sampling valve to ensure consistency of results. Syringe samples were taken directly downstream of the heat shield and the results were compared to samples taken through the sampling valve to ensure that no further reaction was taking place in the downstream piping. The concentrations of VOCs at the reactor inlet were measured by injecting a sample into the gas chromatograph. Conversions were calculated by measuring the VOC concentration at both the inlet and outlet of the reactor. All experiments were run at a pressure of ~2 psig (13.8 kPa) to provide sufficient flow of exhaust gas to the gas chromatograph.

Results

We have examined the catalytic incineration of toluene, chlorobenzene, acetonitrile, and thiophene at a variety of concentrations, residence times, and methane concentrations. We chose these compounds because they either represent common solvents or contain species that are known to cause poisoning in other catalytic systems.

The incineration of methane without the addition of any VOCs was first examined to provide a basis for comparison for later experiments. The case we examined was the incineration of methane at a concentration of 6.5% in air at a combustion temperature of 1,240°C at a residence time of ~ 4 ms. The exhaust compositions for this experiment were measured using Thermo-Environmental Instruments hydrocarbon (HC), carbon monoxide (CO), and NO*x* detectors. Exhaust concentrations of unburned hydrocarbons, CO, and NO*x* were found to be 6 ppm, 0.2 ppm, and < 0.01 ppm, respectively. It is most important to note the high conversion of methane ($> 99.9\%$) and the very low NO*x* (< 0.01 ppm) production observed in this experiment.

The incineration of methane was then examined at a concentration of 6.75% in air in the apparatus described in the experimental section. In the second experiment, inlet gas flow rates were varied from 2 to 5 std. L/min (sLpm) resulting in residence times (τ) of 4 to 12 ms. Methane concentrations in the exhaust were found to be less than 5 ppm for all experiments. Temperatures observed during the experiment are shown in Figure 3a, along with the calculated adiabatic temperature for this composition. The observed increase in catalytic temperature with flow rate indicates that the catalyst operates more nearly adiabatic as the flow rate increases. We have shown previously that the minimum catalyst temperature where combustion of pure methane in room-temperature air can take place in this type of a reactor configuration is approximately 1,050°C at a concentration of ~ 5.75% methane in air for a Pt catalyst (Goralski and Schmidt, 1996).

Blank experiment

A blank-run experiment was performed to see what would happen if a plain Al_2O_3 monolith were placed in the reactor instead of a monolith coated with a catalyst. A single plain Al_2O_3 monolith was placed in the reactor in the same manner as described previously with a catalyst. The inlet to the reactor was set at 6.5% methane in air and a flow rate of 3 sLpm. The monolith was then heated with a Bunsen burner until it was observed to be glowing. The reactor was then insulated and the Bunsen burner was removed. The reactor was observed to operate autothermally, but only for a period of ~10 min until it extinguished. It was observed that the upstream face of the monolith began to cool, and this propagated through the monolith until it completely extinguished. The conversion of methane was measured to be only ~ 80%. The temperature could not be accurately measured due to wild fluctuations in the thermocouple readout. These fluctuations were caused by the thermocouple igniting and extinguishing heterogeneously in the reacting atmosphere downstream of the monolith.

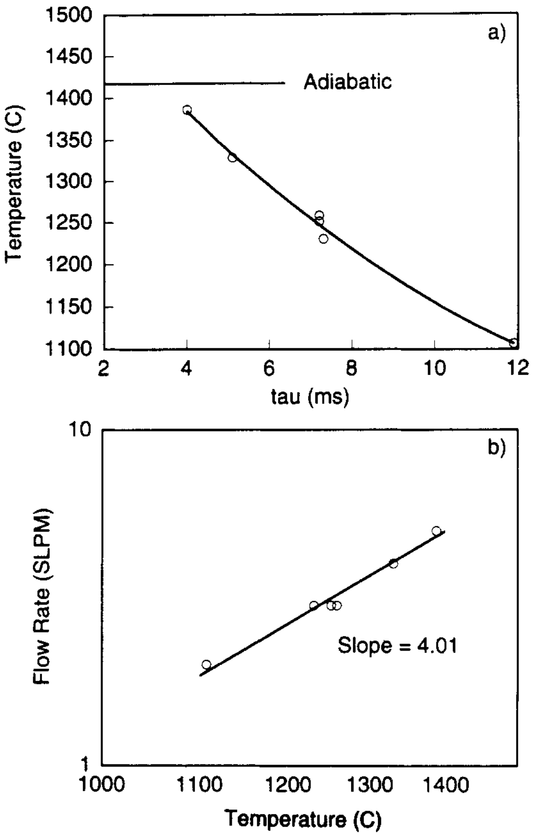

Figure 3. Temperature as a function of residence time for combustion of 6.75% methane in air over a platinum-coated alumina monolith.

Toluene

The incineration of toluene was first examined at a flow rate of 3 sLpm ($\tau = 7$ ms) at a methane concentration of 6.75% over both Pt and Pd catalysts. The toluene concentration in the feed was varied from 500 ppm to 2,000 ppm by volume. The results of these experiments are plotted in Figure 4. Figure 4a shows both the outlet concentration of toluene (lower curves) and calculated conversion for both the Pt and Pd catalysts. The outlet concentration of toluene for the Pt catalyst was constant at ~ 0.2 ppm, while the exhaust from the Pd catalyst varied from ~ 0.7 ppm to 0.4 ppm. The resulting conversion for each of these cases exceeds 99%, as is shown in Figure 4a, with Pt demonstrating slightly higher conversion. The measured catalyst temperature for these experiments is shown in Figure 4b. The Pt catalyst had a temperature that was ~10°C hotter than the Pd catalyst over the range of inlet concentrations examined. Because Pt was found to be slightly superior to Pd in terms of the observed conversion, the remainder of the results presented here are for Pt catalysts.

The flow rate to the reactor was then varied to determine if the residence time in the reactor has an effect on the concentration of toluene in the exhaust. The gas flow rate fed to the reactor was varied from 2 sLpm to 5 sLpm, which corresponds to residence times of 4–12 ms, as the inlet concentration of toluene was varied from 500 ppm to 2,000 ppm. Figure 5a shows both the concentration of toluene in the ex-

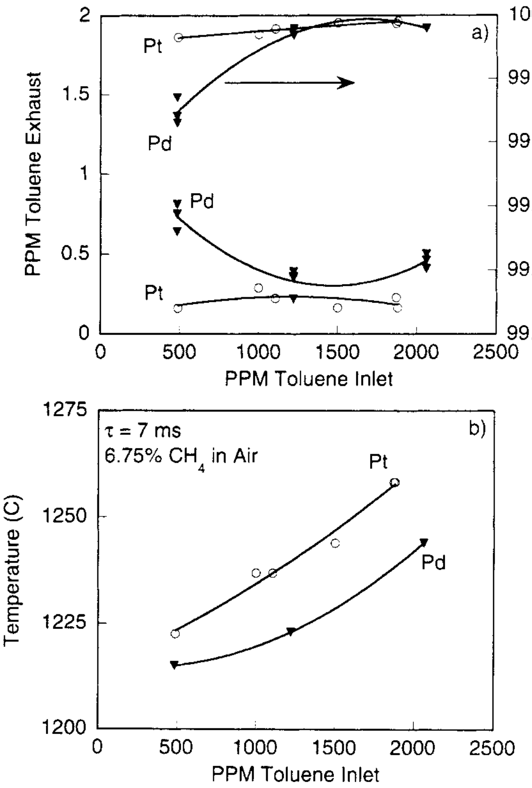

Figure 4. Incineration of toluene over Pt and Pd catalysts at a residence time of 7 ms and methane concentration of 6.75% methane in air.

(a) Outlet concentration and conversion vs. inlet concentration of toluene. (b) Temperature vs. inlet concentration of toluene.

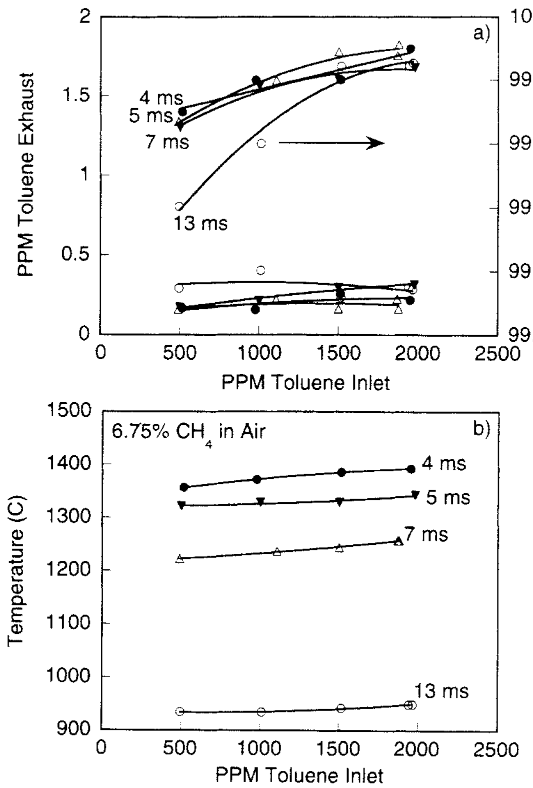

Figure 5. Incineration of toluene in air over a platinum-coated monolith at a methane concentration of 6.75% methane in air.

(a) Outlet concentration of toluene and conversion vs. inlet concentration of toluene at various residence times. (b) Temperature vs. inlet concentration of toluene at various residence times.

haust as well as the calculated conversion as the residence time was varied from 4 ms to 13 ms. The outlet concentration of toluene remained essentially constant at 0.2–0.4 ppm, as the residence time was varied from 4 to 12 ms. This corresponds to conversions of 99.96–99.98%. The data show that the conversion is slightly lower for lower inlet concentrations, because the outlet concentration is approximately constant, resulting in a lower calculated conversion.

The catalyst temperature as a function of the toluene inlet concentration and flow rate is shown in Figure 5b. This plot shows that there is a small increase in temperature as the amount of toluene in the feed is increased, as well as a larger increase in temperature as the flow rate is increased. These data show the same general trend with flow rate as shown in Figure 3a, which shows the temperature dependence upon flow rate for the combustion of methane alone.

Also investigated was the effect the methane concentration had on the conversion and outlet concentration of toluene. During this experiment, the methane concentration in the reactor feed was varied from 7% to 5.5%, while the inlet concentration of toluene was held constant at 1,000 ppm. For these experiments the residence time was held constant at ~ 7 ms. At methane concentrations below 5.5%, the catalyst was observed to remain ignited for short periods of time before it extinguished. Figure 6a shows both the conversion (upper curve) and outlet concentration (lower curve) of toluene as a function of methane concentration. The outlet concentration of toluene remained essentially constant between 0.2 and 0.4 ppm as the feed concentration of methane was varied from 5.5% to 7%. Figure 6b shows the temperature of the catalyst during this experiment. The catalyst temperature was found to increase nearly linearly from 1,120°C to 1,260°C as the concentration of methane was increased from 5.5% to 7%.

Chlorobenzene

The incineration of chlorobenzene was then examined at a flow rate of 3 std L/min ($\tau \sim 7$ ms) for inlet concentrations of chlorobenzene ranging from 500 ppm to 2,000 ppm. The methane concentration was held constant at 6.75%. Figure 7a shows how the outlet concentration of chlorobenzene was found to vary with the inlet concentration. It was found that the chlorobenzene concentration remained relatively constant at ~ 0.2 ppm as the inlet concentration was varied from 500 ppm to 2,000 ppm. This corresponds to a conversion of ~ 99.97%, as shown in Figure 7b. The catalyst temperature remained constant at ~1,225°C as the inlet concentration of chlorobenzene was varied from 500 ppm to 2,000 ppm. It was observed that the catalyst operation was very stable for periods of up to 8 h of continuous operation (the outlet concentration of toluene remained the same). There was no apparent poisoning of the catalyst from the chlorine in the chlorobenzene. We also found that varying the residence time

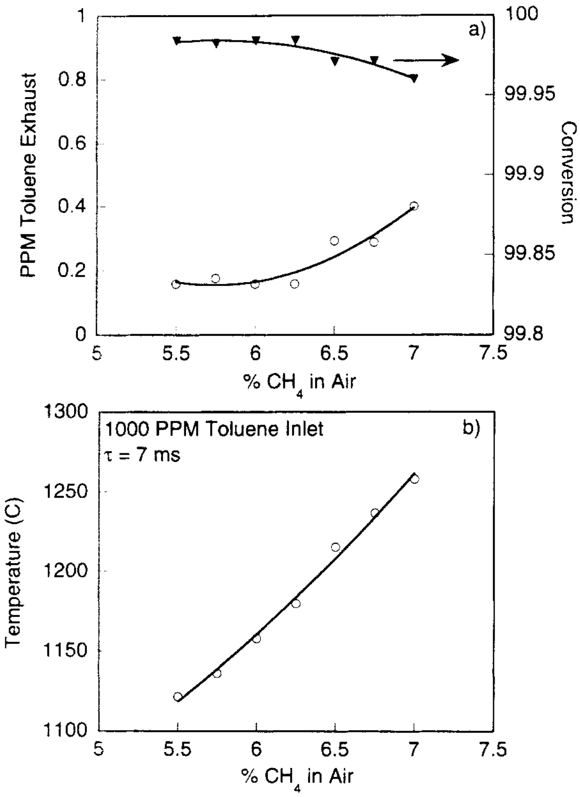

Figure 6. Incineration of 1,000 ppm toluene in air over a platinum-coated monolith at a residence time of 7 ms.

(a) Conversion and outlet concentration of toluene vs. inlet concentration of methane. (b) Temperature vs. inlet concentration of methane.

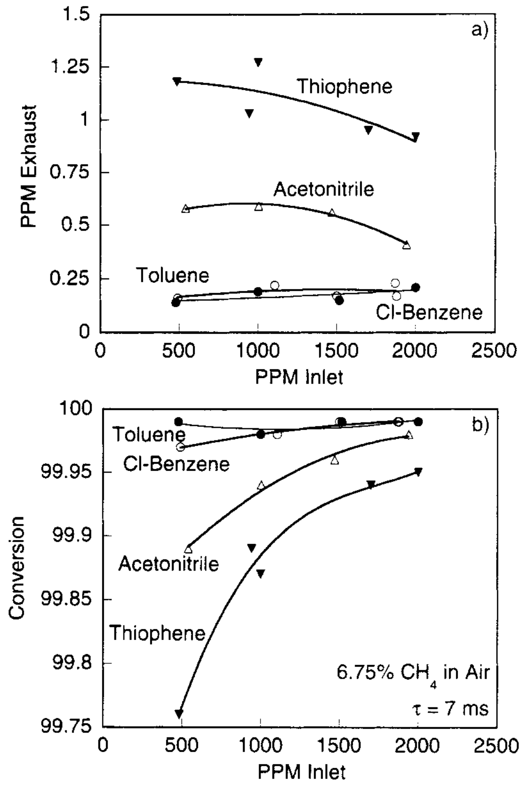

Figure 7. Incineration of toluene, chlorobenzene, acetonitrile, and thiophene in air over a platinum-coated monolith at a methane concentration of 6.75% and a residence time of 7 ms.

(a) Outlet concentration vs. inlet concentration. (b) Conversion vs. inlet concentration.

from 4 ms to 7 ms and the methane concentration from 6% to 7% had no apparent effect on the outlet concentration of chlorobenzene, although the reactor operated at a higher temperature at shorter residence times. These trends are as consistent as those seen for the incineration of toluene.

Acetonitrile

The incineration of acetonitrile was examined under the same operating conditions used in the chlorobenzene experiments. The outlet concentration and conversion are shown as a function of inlet concentration in Figures 7a and 7b. It was found that the outlet concentration of acetonitrile remained almost constant at 0.5 ppm as the inlet concentration of acetonitrile was varied from 500 ppm to 2,000 ppm. This results in a conversion of > 99.9% for all cases examined. The catalyst temperature was found to be slightly higher than the temperatures observed for the incineration of toluene and chlorobenzene. During the experiment the catalyst temperatures ranged from 1,260°C to 1,270°C as the inlet concentration of acetonitrile was increased from 500 ppm to 2,000 ppm. Again, the outlet concentration and conversion of acetonitrile was observed to be independent of the residence time and methane concentration.

Thiophene

The incineration of thiophene was examined last. The experimental conditions were a flow rate of 3 sLpm ($\tau \sim 7$ ms), methane concentration of 6.75%, and a varying thiophene inlet concentration from 500 ppm to 2,000 ppm. Thiophene was found to have the highest outlet concentration and catalyst temperature of the four compounds examined. Figures 7a and 7b show how the outlet concentration and conversion varied as a function of the inlet concentration. The outlet concentration varied from ~1.0 ppm to 1.3 ppm as the inlet concentration was increased from 500 ppm to 2,000 ppm. The temperature was found to increase from 1,280°C to 1,290°C as the concentration of thiophene in the inlet gas was increased from 500 ppm to 2,000 ppm. No apparent catalyst deactivation was observed from sulfur poisoning.

Discussion

Mechanism

The reaction mechanism in a conventional catalytic incinerator is primarily heterogeneous combustion because low temperatures and lean compositions allow for very little homogeneous reaction, even at the relatively long residence times used in those systems. Thermal incinerators, on the other hand, operate almost purely homogeneously, with small heterogeneous contributions from the walls or packing in the combustion chamber. The short-contact-time incinerator discussed here most likely operates with a combination of heterogeneous and homogeneous mechanisms.

We have done simple modeling with complete homogeneous combustion chemistry to try to ascertain how much homogeneous reaction is taking place in this system. Assuming an isothermal plug-flow reactor and the 277 reaction GRI mech 2.11 (Bowman et al., http://www.me.berkeley.edu/gri_mech/), for methane combustion chemistry, we have modeled our reactor at several operating conditions to see if the high conversions that we observed at residence times on the order of several milliseconds can be described by homogeneous chemistry. GRI mech is an optimized methane oxidation mechanism including nitrogen reactions to predict the formation of nitrogen oxides. The optimization targets for NO reactions include modeling flow reactors at temperatures between 900 and 1,400 K, which is well within the temperature range examined here.

We examined the conversion of methane and NO*x* formation as a function of residence time for four cases that correspond to the residence times and temperatures seen in the toluene incineration experiments. The times and temperatures we examined were (1) 4 ms, 1,350°C; (2) 5 ms, 1,300°C; (3) 7 ms, 1,200°C; and (4) 12 ms, 900°C. All results are at a composition of 6.75% methane in air. The results for cases 1, 2, and 3 are shown in Figure 8a. This figure shows that homogeneous chemistry does in fact predict complete conversion of methane for the high temperatures and residence times observed in these cases. The results of case 4 are plotted in Figure 8b. In this case, we see that the model only predicts conversion of ~ 0.8% for a residence time of 12 ms. These results indicate that there must be heterogeneous chemistry taking place in the low-temperature experiments to account for the nearly complete conversion observed experimentally. It is still unclear, however, what is happening in the high-temperature experiments, because the homogeneous chemistry does in fact predict high methane conversions.

In order to better understand the high-temperature regime, we examined the initial methane combustion experiment to see how the outlet composition predicted by the model matched the outlet composition from the experiments. The conditions modeled were a methane concentration of 6.5% methane in air and a temperature of 1,240°C. The results are plotted in Figure 9. Figure 9a shows the conversion and NO level as a function of residence time, and Figure 9b shows the CO concentration in parts per million vs. residence time. It is clear that the homogeneous mechanism predicts significantly higher amounts of NO*x* and CO than were observed in the experiments. The model predicts an output concentration of CO of nearly 100 ppm, where the experiment showed less than 1 ppm. In addition, the model predicts an NO concentration of ~ 6 ppm, where less than 0.1 ppm was observed in the experiment.

This model suggests that the mechanism for methane combustion in this reactor is primarily heterogeneous. One mechanism by which nitrogen oxides are formed in combustion environments is by the reaction of fuel radicals with diatomic nitrogen. The very low levels of NO*x* observed in our experiment are one indication that the mechanism is primarily heterogeneous. The heterogeneous reactions are sufficiently fast that they do not allow for the formation of significant amounts

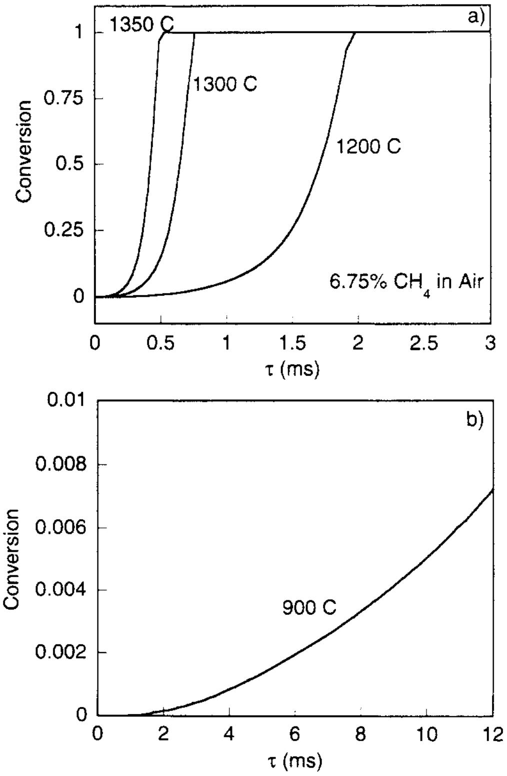

Figure 8. Isothermal modeling results for combustion of 6.75% methane in air.

(a) Conversion vs. residence time for temperatures of 1,350, 1,300, and 1,200°C. (b) Conversion vs. residence time for temperature of 900°C.

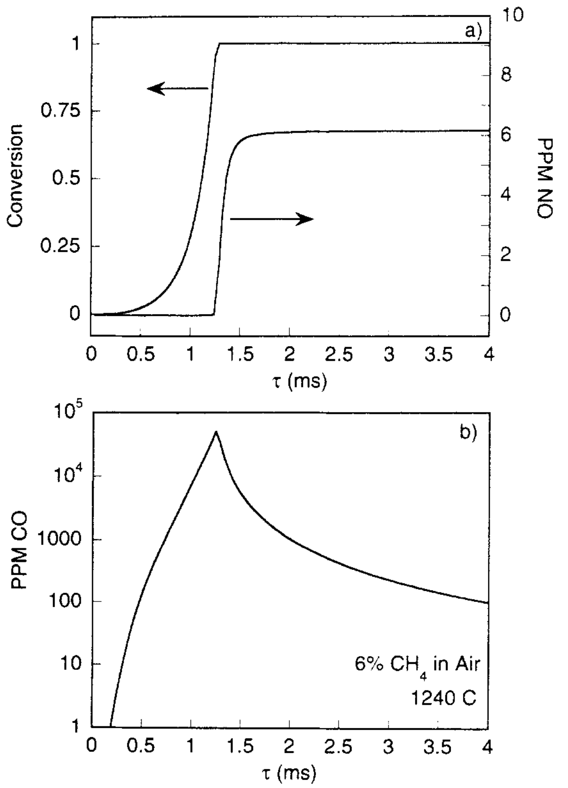

Figure 9. Isothermal modeling results for combustion of 6.5% methane in air at 1,240°C.

(a) Conversion (upper curve) and ppm NO (lower curve) vs. residence time. (b) ppm NO vs. residence time.

of radicals in the gas phase that can lead to the formation of NOx, because the fuel is consumed quickly at the catalyst surface.

While this model helps to explain the methane combustion, it provides little insight into the mechanism for the reactions of the VOCs. Unfortunately, there are no detailed mechanisms available for the combustion of these compounds. However, these molecules are significantly more reactive than methane and should undergo heterogeneous as well as homogeneous reaction much more readily than methane.

The mechanism of reaction in the short-contact-time catalytic appears to be the heterogeneous combustion of the methane fuel combined with the heterogeneous and homogeneous reaction of the more reactive volatile organic species. The high temperatures caused by the heterogeneous reactions will allow the VOC molecules to react very quickly in the gas phase as well as on the surface of the catalyst. This is evidenced both by the modeling results, which show that homogeneous chemistry cannot fully explain the experimental results, as well as by the blank-run experiment where a noncatalytic monolith would not remain ignited under the same operating conditions as the catalytic monolith.

Destruction efficiency

The experiments performed in the laboratory show that the destruction efficiency (DE) of VOCs using the short-contact-time catalytic incinerator is very high. The destruction efficiency for all cases examined was 99% or more with all methane concentrations at the incinerator outlet 5 ppm or less. The emissions of NOx and CO were only measured at one operating condition without the presence of VOCs in the inlet stream. However, they were found to be <0.2 and <0.01 ppm, respectively.

Residence-time distribution

The short-contact-time catalytic incinerator has a much narrower residence time distribution than either conventional catalytic or thermal incineration systems because there is almost no backmixing in this system. Thermal incinerators often have significant amounts of backmixing, which leads to temporal and spatial temperature variations in the reaction chamber. This can lead to the formation of NOx and partial oxidation products such as formaldehyde and CO because of local high temperature, rich composition, or short time regions within the reaction chamber. Low-temperature catalytic oxidation systems using extruded monolith supports often have blank or clogged channels, again leading to cool spots and nonuniform flow profiles within the catalyst bed. The very tight residence time distribution, open-pore structure, and high heat transfer of a short-contact-time catalytic incinerator leads to very uniform temperatures and tight product distributions.

Heat loss

Radiation is the dominant mechanism of heat loss in this reactor. A simplified energy balance for the reactor could be written as

$$Q \cdot H_{\text{in}} = Q \cdot H_{\text{out}} + A \cdot \epsilon \cdot \sigma \cdot T^4 + UA'(T - T_{\text{surr}}), \quad (1)$$

where H_{in} and H_{out} are the total enthalpies of the reactants and products; Q is the flow rate; A and A' are the radiative and conductive heat-transfer areas; ϵ is the emissivity of the reactor; σ is the radiative heat-transfer coefficient; and T and T_{surr} are the temperature of the reactor and the temperature of the surroundings, respectively. By bringing the enthalpy out of exhaust to the lefthand side, taking the logarithm of both sides, and combining some constants, this equation can be written as

$$\log[Q(H_{\text{in}} - H_{\text{out}})] = \log(C_1 \cdot T^4 + C_2 \cdot T + C_3), \quad (2)$$

where C_1, C_2, and C_3 are constants. The first and second terms in this equation are much larger than the third term (C_3) since the catalyst temperature is much greater than the temperature of the surroundings, so C_3 may be neglected. The dominant mechanism of heat loss can then be determined by plotting the log of the flow rate as a function of the log of the temperature and determining the slope. A slope of one would indicate that conduction is the dominant mechanism of heat loss, while a slope of four would indicate that radiation dominates.

Figure 3b shows the log of the flow rate vs. the log of temperature. The curve is nearly linear with a slope of 4.01, indicating that radiation is in fact the dominant mechanism of heat loss.

Temperature

This reactor operates at temperatures significantly higher (900–1,400°C) than temperatures in conventional catalytic incinerators (300–650°C), but much cooler than the peak temperatures seen in thermal incinerators ($>1{,}500$°C). Operating in this temperature range is advantageous for several reasons. At higher temperatures the reaction rates increase dramatically, allowing high conversion at much shorter contact times. The overall reaction rate in the short-contact-time reactor is limited by the rate of bulk mass transfer of reacting species to the surface of the catalyst because of the high surface reaction rates at the elevated temperatures where this reactor operates.

It is important to maintain a high reactor temperature to ensure that the catalyst remains ignited. Experiments have shown that for the combustion of pure methane in air a minimum catalyst temperature of ~1,050°C is necessary to ensure that the catalyst remains ignited. Experiments with toluene present in the feed have shown that cooler operation is possible. A reactor temperature of 1,100°C should be considered a lower operating limit. It is also important to ensure that the temperature in the reactor does not exceed 1,600°C, where the alumina support begins to degrade and become very fragile. Temperatures below 1,500°C must also be maintained in order to prevent the formation of NOx, which can become significant above this temperature.

We do observe stable operation at 900°C with 1,000 ppm toluene and 6.75% methane in air, which is cooler than the previously reported extinction temperature for this type of catalyst combusting pure methane, but the residence time in this case is longer (13 ms) than the residence time (5 ms) in the previously reported experiment. This could result in a more uniform radial temperature profile across the catalyst, resulting in higher temperatures at the edge of the catalyst. It is observed that these catalysts tend to extinguish from the edges in, although the temperature is measured at the center of the downstream face of the catalyst. Because of this mechanism of extinction, a more uniform temperature profile would result in a lower measured extinction temperature. This lower temperature operation could also be the result of the more reactive toluene species acting to enhance the reactivity of the catalyst by supplying radical species to the catalyst surface in a regime where the less reactive methane molecules would not otherwise react.

The optimum operating temperature for a larger-scale short-contact-time catalytic incinerator should be approximately 1,200°C. This temperature is high enough that there should not be a problem with either catalyst extinction or NOx production. This corresponds to operation at ~6% methane in air, depending on the fuel value of the VOC stream to be incinerated as well as heat losses from the reactor. It is very important to note that this fuel requirement could be further reduced by utilizing exhaust gas preheated to use the sensible heat of the exhaust stream to preheat the inlet gases, as sketched in Figure 1. This system would also be much more thermally efficient if the reactor were constructed to minimize radiant heat losses.

Catalyst lifetime

There are several issues that could affect the lifetime of a catalyst in this type of reactor. The results of these experiments indicate that there is no problem with chemical degradation by catalyst poisons on the time scales we examined. Thermal degradation could affect this catalyst in two ways, by degradation of the support or loss of metal by evaporation or other mechanisms.

Operation at temperatures in excess of 1,600°C has been shown to cause brittleness of the catalyst. This is because the monoliths consist of 92% α-Al_2O_3 with 8% SiO_2 present as a stabilizer. At elevated temperatures, the grain size of the Al_2O_3 particles increases, leading to embrittlement of the monolith. This is not a major problem as long as the monoliths are not subjected to excessive handling or mechanical stress.

The biggest concern for long-term durability of the catalyst is loss of platinum. There are several mechanisms by which platinum can be lost from the surface of the monolith. One of these is the direct evaporation of platinum into the gas phase. McCarty et al. (1996) have shown, using thermodynamic calculations of vapor pressure, that platinum does not evaporate as fast as PtO_2 and PtOH in oxidizing atmospheres in the presence of water. These calculations were done in atmospheres of 50% oxygen and 50% water. It is not clear how these results translate into the actual metal loss that would be seen in a system such as the one described here, since the calculations were done in different atmospheres in nonreacting systems.

The results reported in this article are all for catalysts with a weight loading of ~5% of platinum. We have demonstrated the use of catalysts with weight loadings as low as 0.41% for combustion of methane, and there was no noticeable difference in performance when compared to catalyst with a loading as high as 7%. We have used individual catalysts up to a cumulative of 200 h without any noticeable loss in activity. It is unclear what the actual rate of metal loss on these catalysts is, because it is very difficult to accurately track the amount of weight loss of the catalyst over time with the experimental system. This is because the mass of platinum on the catalyst is so low that the loss of even a small piece of the catalyst that may get broken off during handling would account for more mass than the entire amount of platinum loaded on the support.

Conclusions

For all experiments described here, very high conversions (> 99.5%) of volatile organic compounds were observed at contact times more than 100 times shorter than those required to obtain this level of conversion in either a thermal or conventional catalytic incinerator. In addition, there was no apparent decrease in performance of the reactor when compounds containing catalyst poisons such as chlorine and sulfur were present in the inlet stream. Preliminary data show that negligible NOx is produced when operating at temperatures near 1,250°C. These results are very promising and suggest that larger scale incinerators could be constructed that would demonstrate enhanced performance over conventional systems.

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