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FLOW TUBE REACTOR STUDIES OF CATALYTICALLY STABILIZED COMBUSTION OF METHYL CHLORIDE

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Catalytically stabilized combustion of methyl chloride ($\phi = 0.035$) was studied at partial through 99.98% conversion in a catalytically coated isothermal 1.6 mm ID tubular reactor at temperatures from 800–1350 K. Results were compared with product profiles from an equivalent non-catalytic reactor. Two catalysts were studied: platinum and manganese oxide. Catalytic stabilization was shown to produce better performance compared to the thermal reactor in terms of temperature and residence time required for a given destruction effectiveness. Catalytic stabilization was also found to alter the reaction kinetics involved as evidenced by different reaction intermediates at partial conversion conditions for each of the two catalysts studied and for the non-catalytic reactor. This provides direct evidence for heterogeneous/homogeneous reaction mechanism coupling in the catalytically stabilized combustion of chlorinated hydrocarbons.

Introduction

The catalytically stabilized thermal (CST) combustor uses catalytic surface reactions to stabilize gas phase combustion. Exothermic surface reactions maintain the walls near the adiabatic flame temperature providing heat and reactive intermediates to the gas phase, igniting and stabilizing essentially plug flow gas phase combustion.[1,2] CST combustion of conventional fuels has been studied by a number of researchers since the mid-1970s, primarily to explore its potential as a lean-burn combustion system to eliminate gas turbine NO_x emissions.[3,4]

Recent work in our laboratory has shown that an adiabatic CST combustor can stabilize plug flow combustion of even heavily chlorinated mixtures, achieving high destruction levels (beyond our detector limits: 99.994%+) of methyl chloride and methylene chloride with very low residence time (5–20 ms) and improved flame stability.[5] In this study, we show that, compared to the equivalent non-catalytic "hot wall" reactor, the catalyst provides *more* than wall heating, significantly lowering temperature requirements for destruction and altering gas phase chemistry. Thus, CST combustion of chlorinated fuels is influenced both by the ability of the catalytic surface to provide a hot wall and by the generation of reactive combustion intermediates. The current work seeks to determine how kinetic effects related to the catalyst affect reactor

performance. Kinetic studies of CST combustion of chlorinated hydrocarbons have not been carried out previously and are expected to differ from results for hydrocarbons because of previously observed differences in both homogeneous[6–8] and heterogeneous combustion chemistry.

Chlorinated hydrocarbon (CHC) fuels are known to be combustion inhibitors when added to hydrocarbon fuels.[6–9] Combustion initiation steps for chlorinated fuels, however, occur more quickly than for their analogue hydrocarbon fuels. This is because the initial decomposition of the fuel molecule is through the breaking of the relatively weak C—Cl bond. Although the initial decomposition of the parent molecule is faster for the chlorinated analogue, the presence of Cl reduces the rate of combustion propagation by scavenging the H radicals that are important for initiation of the chain branching steps, and the inhibition effect is more a function of the total chlorine content of the mixture than the chlorinated fuel structure. Methyl chloride (CH_3Cl) was chosen as the fuel for this initial study because of its simple structure and because literature data is available for homogeneous oxidation.

Because free radical chain branching is important in gas phase combustion, catalysts which promote radical production would be expected to increase the gas phase reaction rate at a given temperature. Various workers[10–11] have demonstrated that free radicals can be desorbed from platinum at relatively low temperatures. Our studies of OH and O concentrations over heated platinum and quartz surfaces[12,13] have indicated that these low rates of

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surface radical production can significantly promote gas phase combustion through chain branching reactions. We hypothesize that catalytic generation of reactive intermediates may act to offset the inhibition effects in chlorinated hydrocarbon combustion.

Experimental description

A small diameter (1.6 mm ID) isothermal tubular reactor was used to study reaction mechanisms important in the CST combustion of CH_3Cl. Platinum and manganese oxide catalysts were investigated. An alumina tube without catalyst coating was used to provide comparison heated wall "thermal" data.

The experimental design has been described in detail elsewhere,[6,14] thus a summary is given here. Air and CH_3Cl are introduced into a mixing chamber prior to the reaction tube, at an inlet pressure of 1.14 ± 0.1 atm. For the reference inlet flow velocity of 170 cm/sec (at 293 K), the hot flow velocity varies between 460 to 770 cm/sec for the range of temperatures studied (800 to 1350 K). This corresponds to a residence time of between 16 and 27 ms in the hot reaction zone. At the exit end of the reaction tube, the reacting gas mixture is quenched and analyzed by gas chromatograph (GC) equipped with a methanizer and a flame ionization detector (FID). The methanizer is used to convert CO and CO_2 to CH_4 for detection by the FID. The FID is sensitive to light hydrocarbons to approximately 0.1 ppm, but is only sensitive to 1–2 ppm for most of the chlorinated hydrocarbons, and 10–20 ppm for formaldehyde.

A 3% SP-1500 80/120 Carbopack B column was used to separate the light chlorinated hydrocarbons. In a second column configuration, the Carbopack column was used in series with a 100/120 Carbosieve S-II column where CH_4, C_2H_2, C_2H_4, C_2H_6, CO and CO_2 were separated.

The reactor tube is fabricated from alumina with dimensions of 1.6 mm I.D. and 3.0 mm O.D. and length of 300 mm. The tube ID is representative of channels in typical CST monoliths. The reactor tube is electrically heated and the axial temperature profile was shown to be uniform to within ±5 K throughout the temperature range of interest, reproducible to within ±3 K.

A CH_3Cl inlet concentration of 5000 ppm (in air) was used for all the experiments in this study. This corresponds to an equivalence ratio of 0.036 and 120 K adiabatic flame temperature rise, allowing near-isothermal operation. The low CH_3Cl concentration also stretches out the combustion "reaction front" so that the partial oxidation product distribution may be analyzed.

The *platinum* coated reaction tube was prepared using H_2PtCl_6 to impregnate the isothermal section of the tube. The tube was heated in a drying oven for 4 hours at 350 K and then calcined in a furnace at 1400 K for 4 hours. This results in a low surface area corresponding to the surface area of CST combustor monolith catalysts exposed to combustor operating temperatures. Catalyst loading was high enough to ensure independence of measured rate on catalyst loading at all operating conditions and after sintering.

Although platinum is not the catalyst of choice for chlorinated organic combustion, evaluation of a platinum catalyst in the present study allows study of the importance of a high surface oxidation rate in CST incineration. Platinum is an effective catalyst; however, unless suitably complexed with another oxide, platinum oxide can be readily volatilized from platinum catalysts at temperatures as low as 773 K.[15] In the presence of chlorine, platinum loss is accelerated by formation of volatile platinum oxychlorides even though non-volatile platinum oxide and oxychloride alumina solid solutions are also formed. It should be noted that the volatility of platinum can be greatly reduced by incorporation into a high temperature stable lattice. In these tests, no detectable drop-off in effectiveness was observed, although platinum loss was likely occurring.

The *manganese* catalyst coated tube was made by a similar procedure using a manganese nitrate $(Mn(NO_3)2:4H_2O)$ solution as the catalyst precursor. Manganese oxide supported on alumina was used for this study because it was found in our previous studies[14] to have high catalytic activity for CH_3Cl destruction and maintain its activity to high temperatures (at least 1700 K for CH_3Cl). According to the literature, no manganese oxides are found to be stable to these temperatures; therefore, it is likely that a manganese oxide/alumina complex may have formed under the catalytic preparation conditions (as is known to be the case for platinum/alumina) and that it was this complex that was responsible for the observed catalytic activity. In addition, although the manganese catalyst was in the form of an oxide compound as prepared, conversion to chlorine compounds in the presence of chlorine is likely. It is known that manganese chlorides are stable in air to temperatures higher than the present experiments. Thus it is possible that manganese oxychlorides formed on the catalyst surface may be the active catalyst species. Determination of the compound stoichiometry will be a focus of future work; in this paper it is referred to as the "manganese" catalyst.

Discussion

Experimental Results for Alumina (Non-Catalytic) Reactor:

A non-catalytic alumina tube reactor was used to provide a baseline to distinguish between heated-

wall effects and true homogeneous/heterogeneous kinetic coupling. Tests were initially performed at different tube diameters and with quartz tubes to verify that there is no significant surface reaction contribution for the oxidation of CH_3Cl in the standard alumina reactor. In these experiments the temperature required for "complete" (99.98%) CH_3Cl conversion in the thermal reactor was considerably higher than required in either catalytic case (see Fig. 1). At temperatures higher than that required for complete CH_3Cl disappearance (>1350 K), no hydrocarbon or chlorinated hydrocarbon partial conversion products were detected. Carbon monoxide, however, still accounted for over ten percent of the converted CH_3Cl at 1350 K and 16 ms residence time. At a reaction temperature of 1300 K, only 50 degrees lower, conversion of CH_3Cl to chlorinated partial conversion products was at the maximum measured value. At this temperature, carbon monoxide accounted for over 50% of the converted CH_3Cl. At partial conversion levels the only chlorinated products detected were vinyl chloride, methylene chloride, and 1,2-dichloroethane. The maximum mole fraction of CH_3Cl converted to each over the temperature range studied was approximately 0.04, 0.002 and 0.0025, respectively.

Experimental Results for Mn Catalyst:

In the catalytic-wall flow tube experiments, as the temperature is raised, mass-transfer-limited surface reactions and, subsequently, gas phase reactions occur, with ignition of gas phase combustion ultimately resulting in the complete combustion of the CH_3Cl. Analysis of reaction intermediates formed and their concentration profiles as a function of temperature illustrates the role that catalysts play in the initiation/quenching of the combustion/oxidation reactions.

In our previous work,[14] a manganese catalyst was shown to be an effective catalyst for the CST combustion of chlorinated organics. As shown in Figure 1, at the standard flow conditions essentially

complete destruction of CH_3Cl was achieved at about 1200 K with the manganese catalyst, a temperature 150 K lower than for the alumina reactor. Figures 2 and 3 show C1 and C2 reaction product concentrations as a function of reactor temperature. All chlorinated organics produced as reaction intermediates at low CH_3Cl conversion dropped to below detection limits at the point where CH_3Cl dropped below detection limits. However, even at 25 K above the complete CH_3Cl conversion temperature, methane, ethane and acetylene still accounted for one percent of the CH_3Cl conversion. In comparison, the alumina reactor produced lower maximum concentrations of these non-chlorinated species, which were destroyed simultaneously with the chlorinated species. High concentrations of C2s produced at partial conversions (most likely from gas phase methyl radical coupling reactions), together with the 150 K lower temperature requirement of the manganese catalytic reactor as compared to the alumina reactor, also suggests that the manganese catalyst functions by releasing methyl radicals formed by extraction of chlorine, thus increasing the gas phase free radical pool and consequently the reaction rates at a given temperature. Surface and gas phase Cl radicals also help increase the initial radical pool through hydrogen abstraction reactions. This is consistent with previous literature on manganese oxides as dehalogenation catalysts. The bond strength of one of the C—H bonds of CH_3Cl at 101 kcal/mol is very close to the C—H bond dissociation energy (104 kcal/mol) of the first hydrogen removed from methane; it is likely that the first reaction step both for the thermal reactor and with the manganese catalyst is the abstraction of chlorine (C—Cl bond strength 84 kcal/mol). This view is also supported by our previous observations in adiabatic reactor and flow tube tests that showed manganese was catalytically active for the combustion of CH_3Cl but was relatively inactive for the combustion of methane. This is also consistent with the disappearance of chlorinated hydrocarbons prior to the disappearance of methane and ethane be-
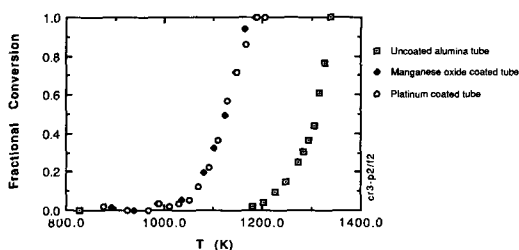

FIG. 1. Comparison of Methyl Chloride Conversion as a Function of Temperature at the Standard Flow Conditions for Alumina, Platinum and Manganese Reactors.
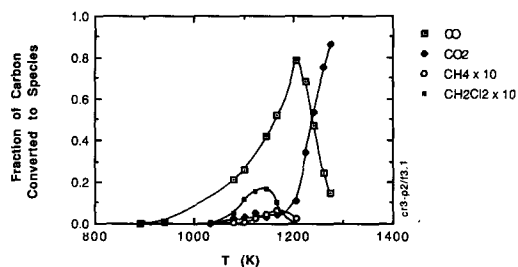

FIG. 2. Conversion of Methyl Chloride to Cl Species in the Manganese Flow Tube Reactor at Standard Flow Conditions as a Function of Temperature.
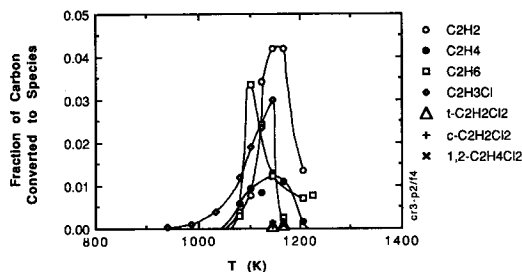
FIG. 3. Conversion of Methyl Chloride to C2 Species in the Manganese Flow Tube Reactor at Standard Flow Conditions as a Function of Temperature.

cause the chlorinated species are converted to hydrocarbons which are subsequently destroyed in the gas phase.

The major initial stable reaction products are carbon monoxide, vinyl chloride and C2 hydrocarbons, with little carbon dioxide formation at low to moderate CH_3Cl conversions (Figs. 1–3). This is an indication that the oxidation reactions are occurring predominantly in the gas phase at the temperatures employed.[16] Inasmuch as manganese oxide is known as a good catalyst for carbon monoxide oxidation,[17] surface combustion would likely produce almost exclusively carbon dioxide.

Reducing residence time from 16 to 5.3 ms (Fig. 4) raised the temperature required for complete CH_3Cl destruction from 1200 K to 1325 K. This was still slightly below the temperature required for very high destruction in the non-catalytic alumina reactor with 16 ms residence time. Varying residence times provided further support for the assumption that the oxidation reactions are predominantly occurring in the gas phase in the manganese reactor. At a reaction temperature of 1200 K, reducing the residence time from 16 ms to 5.3 ms
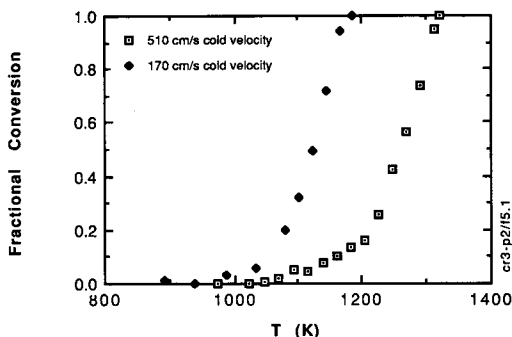

FIG. 4. Comparison of Methyl Chloride Conversion as a Function of Temperature for Cold Flow Velocities of 170 cm/sec and 510 cm/sec in the Manganese Flow Tube Reactor.

lowered the CH_3Cl conversion from better than 99.98% to less than about 20%; at 1150 K this residence time reduction reduced CH_3Cl conversion from greater than 70% to only about 10%. This behavior is compatible with a free radical gas phase reaction mechanism but is incompatible with an isothermal surface reaction mechanism. Surface reaction rate at a given surface temperature is primarily a function of the surface concentration of reactants. Therefore, increasing flow rate would increase the number of moles converted per unit surface area, and thus conversion due to surface reaction observed in the gas phase will drop by less than the decrease in residence time.

The manganese reactor also produces much higher yields of methylene chloride (dichloromethane) at lower CH_3Cl conversion than the noncatalytic alumina reactor (a factor of 20 greater peak concentration). This is suggestive not of surface disproportionation reactions (methane concentrations are too low) but instead of a high gas phase concentration of chlorine atoms resulting in chlorine addition to CH_2Cl. Surface reactions do, however, play a predominant role in methylene chloride production in the manganese reactor. This is indicated both by minimal production of methylene chloride in the alumina reactor and by the observation that the maximum mole fraction conversion of CH_3Cl to methylene chloride dropped by less than a factor of three (from about 0.017 to 0.008) with a threefold reduction in the residence time. This is consistent with our hypothesis that the methyl chloride conversion is initiated by decomposition to methyl and chlorine radicals by the catalyst and that the surface generated chlorine radicals are important in methylene chloride production.

At moderate CH_3Cl conversions (between 1125 and 1175 K), cis- and trans-1,2-dichloroethylene were detected. This is likely a reflection of the higher methyl radical and chlorine concentrations produced in the manganese catalyst tests as compared to the alumina tube tests due to the activity of the manganese catalyst for dehalogenation of CH_3Cl. Dichloroethylene is formed subsequent to 1,2 dichloroethane (Fig. 3), which is predominantly formed through CH_2Cl recombination. CH_2Cl is formed through reaction of Cl and CH_3 with CH_3Cl. Dichloroethylene is possibly formed via surface dehydrogenation of dichloroethane.

A detectable concentration of carbon monoxide was observed even at a temperature of 1275 K or about 75 K higher than the temperature for elimination of detectable chlorinated organics. This is similar to the alumina reactor results, and is a preliminary indication that monitoring of reactor effluent carbon monoxide concentrations in this particular system may provide a measure of chlorinated hydrocarbon destruction effectiveness for application of control strategies.

Results for the Platinum Catalyst:

In the platinum catalyst experiments at the standard flow conditions, the nominal temperature of complete CH_3Cl conversion was 1200 K, the same as that of the manganese catalytic reactor and, again, 150 K below that of the alumina thermal reactor. Examination of intermediate species formed at low CH_3Cl conversion in the platinum coated reactor tube tests, Figs. 5 and 6, shows that in addition to the chlorinated partial conversion species produced in the thermal tests, measurable amounts of chloroform (not found in manganese catalyst experiments) and cis- and trans- 1,2-dichloroethylene were produced. Unlike in the manganese reactor experiments, no methane, ethane, ethylene or acetylene were detected, likely because of the high oxidation activity of platinum. The platinum catalyst also produced over fifty times the maximum concentration of methylene chloride observed in the thermal tests and ten times as much as the manganese catalyst tests. The relatively high methylene chloride yield at low CH_3Cl conversion can be explained by a high activity for surface disproportionation reactions on the platinum catalyst, yielding methylene chloride and also chloroform. In contrast, vinyl chloride concentrations were an order of magnitude lower than in either the thermal or manganese experiments. This low vinyl chloride production would appear to be related to essentially complete surface combustion of the CH_3Cl, at a lower temperature than in the non-catalytic experiments. Vinyl chloride is formed in the gas phase primarily through recombination of CH_2Cl. Maximum 1,2 dichloroethane concentrations, however, were about the same as in the thermal tests and the production of cis- and trans- 1,2 dichloroethylene was about the same as in the manganese tests.

Examination of the data for carbon monoxide and carbon dioxide production in the platinum flow reactor (Fig. 5) demonstrates that, with the platinum catalyst, surface oxidation reactions are responsible
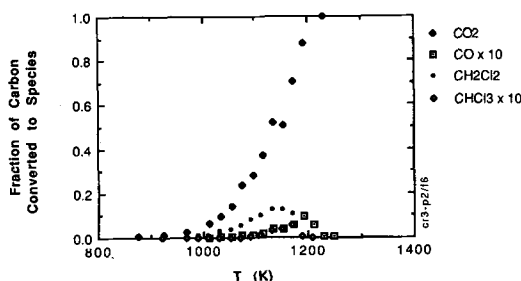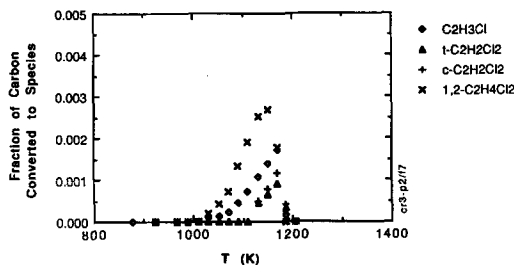

FIG. 6. Conversion of Methyl Chloride to C2 Species in the Platinum Flow Tube Reactor at Standard Flow Conditions as a Function of Temperature.

for initial CH_3Cl conversion directly to carbon dioxide. As noted above, a high ratio of carbon dioxide to carbon monoxide at low conversions is an indication of surface catalyzed reactions. However, in view of the relatively high volatility of platinum as platinum oxychlorides, the possibility exists that carbon monoxide conversion to carbon dioxide is catalyzed by volatilized platinum in the boundary layer. Note that the high destruction levels of chlorinated organics found at the higher temperatures indicate that gas phase reactions are important in achieving the ultimate high conversions obtained.

Comparison of Catalytic and Thermal Oxidation:

As shown by Fig. 1, both the manganese and the platinum catalytic reactors were equally effective in destroying CH_3Cl, and both catalysts achieved essentially complete conversion of CH_3Cl at a 150 K lower temperature than did the thermal experiments at equivalent residence time. The essentially complete destruction achieved at modest temperatures demonstrates that efficient gas phase combustion in millisecond residence times is possible at much lower temperatures in a CST combustor than in an equivalent heated-wall reactor. This indicates that the catalyst plays a greater role in combustion stabilization than merely the maintenance of a hot wall. This is more apparent by the difference in intermediate product distributions at low CH_3Cl conversion in the alumina, platinum and manganese flow tube reactors. These differences result from difference in catalytic reaction products, with predominantly methyl and chlorine radicals produced from the manganese surface and CO_2 and H_2O from the platinum surface, as well as possible other labile intermediates. Intermediate product profiles are important in that they can be used to predict emissions that might occur during unsteady state operation.

The equivalent activity of the manganese and

FIG. 5. Conversion of Methyl Chloride to C1 Species in the Platinum Flow Tube Reactor at Standard Flow Conditions as a Function of Temperature.

platinum catalysts for destroying CH_3Cl is intriguing inasmuch as the intermediate products are different. This indicates that the same process is likely rate determining in both cases. One possibility is that CH_3Cl destruction in both systems is initiated by chlorine carbon bond cleavage on the surface of either catalyst which controls the temperature for ignition of mass transfer-limited surface production of reactive intermediates which vary according to catalyst used (CH_3 for Mn and CO_2, H_2O and OH for Pt).

Complete oxidation is controlled by ignition of gas phase combustion in all systems tested as evidenced by the sharp increase in CH_3Cl conversion as high conversion temperatures are approached. This is not consistent with complete conversion taking place through mass-transfer-limited-surface oxidation reaction as this would be a relatively temperature insensitive process. Thus, albeit by differing paths, both catalysts act to initiate gas phase combustion at temperatures lower than those achievable in thermal systems.

Conclusions

Experimental results using either platinum or manganese-based catalysts showed the catalytic reactor attained nominally complete conversion at a temperature well below that required for a non-catalytic heated-wall reactor. Evidence of methyl radical coupling products in the gas phase at low CH_3Cl conversion and CO as the primary initial oxidation product indicate that the manganese catalyst is acting primarily as a dehalogenation catalyst, supplying CH3 radicals to the gas phase. The reaction pathway is altered by the surface reactions as evidenced by the differences in the concentration and identity of reaction intermediates at temperatures below that required for complete conversion at this residence time. Experimental results using a platinum reactor produced similar destruction effectiveness results to the manganese case. Compared to the manganese results, a different promotion mechanism was observed, as evidenced by markedly different intermediate product profiles at partial CH_3Cl conversions. The initial product observed in the platinum reactor case was carbon dioxide indicating that this catalyst was acting primarily as a deep oxidation catalyst.

Beyond the specifics of determining reaction mechanisms, this work highlights a number of principles relating to catalytically stabilized incineration of chlorinated hydrocarbons. Without catalytic effects, externally maintaining the flow reactor walls at moderately high temperatures can be sufficient (with adequate mixing and adequate preheat) to achieve high destruction effectiveness of a chlorinated fuel. The use of catalytic stabilization, how-

ever, can significantly improve upon plug flow tubular reactor (PFTR) hot wall reactor performance. First, a non-catalytic PFTR would require wall heating or exhaust heat regeneration to maintain a given wall temperature. In an adiabatic CST combustor, catalytic reactions maintain the walls near the adiabatic flame temperature even prior to the onset of gas phase ignition. In addition, the catalyst provides reactive intermediates which lower the temperature required for a given destruction effectiveness. This catalytic temperature advantage, being surface reaction driven and therefore mass transfer limited, increases with reduced residence time (alternately expressed as increased throughput) because as gas phase residence time decreases the *relative* contribution from surface effects increases.

Thus complex homogeneous/heterogeneous reaction mechanism coupling, initiated by the reactivity of the catalyst, is a primary contributor to stabilization of CST combustion of CH_3Cl. Future studies will focus on detailed kinetic investigation of this coupling to assist in design of CST combustors for chlorinated hydrocarbon incineration.

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