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Catalytic Combustion in Internal Combustion Engines: A Possible Explanation for the Woschni Effect in Thermally-Insulated Diesel Engines

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13. ABSTRACT (Maximum 200 words)

This report describes research undertaken to determine if catalytic combustion effects occur with the use of zirconia (ZrO_2) thermal barrier coatings (TBCs), or other coatings, in diesel engines, and if so, whether these effects have significant impact upon engine combustion, fuel economy, or pollutant emissions. A simple furnace system was used to identify catalytic combustion effects in the ignition and combustion of propane/air mixtures over catalyst-doped m-ZrO_2 spheres. Three classes of catalysts were examined: zirconia-stabilizing oxides (CeO_2, Y_2O_3, MgO), transition metal oxides (Co_3O_4, Cr_2O_3, Fe_2O_3), and noble metals (Pt). Each class exhibited characteristic combustion effects, with the ignition temperature increasing, e.g., from approximately 200°C for Pt to 550°C for the stabilizing oxides. The results suggest that the Woschni effect, a controversial phenomenon wherein thermal-insulating measures are postulated to actually increase heat transfer from the diesel combustion chamber, may be only a manifestation of catalytic combustion. Previous research on catalytic combustion in internal combustion engines is briefly reviewed and discussed. An earlier version of this report is to be published in J. Surface and Coatings Technology as "Catalytic Combustion Effects on m-ZrO_2 Doped with Various Metal Nitrates."

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1. Introduction

Low heat rejection (LHR) diesel engines using zirconia-based thermal barrier coatings (TBCs) were proposed in the past as a means for eliminating the radiator, water pump, etc., from military land vehicles, and obtaining an overall fuel savings of up to 30-40% [1]. However, a range of engine fuel economy effects, varying from being 10-15% better to 7-8% worse, has since been reported from different laboratory and in-service engine tests. Among the most recent literature, the results of some groups show no benefit [2], while others suggest that perhaps up to ~5% improvement in fuel economy might be possible, albeit requiring turbo-compounded engines [1,3-5]. An analysis by Amann [6] indicates that, speaking strictly in terms of engine combustion performance, an increase of only a few percent in fuel efficiency can be expected for LHR engines.

From laboratory engine studies, a number of specific difficulties have been identified with TBCs (or thermally insulated engines), these being that: 1) they can adversely affect certain aspects of the combustion process, including volumetric efficiency, ignition delay timing and fuel/air mixing [4], and 2) that they seem, in some cases, to actually increase the rate of heat rejection from the combustion chamber, as described by Woschni et al [7,8]. As will be discussed below, it may be possible that catalytic combustion effects at the TBC surface are involved in some of these problems.

The effect of TBCs on diesel emissions is also uncertain, with nitrogen oxide (NO_x) emissions being reported as increased in some tests, but reduced in others. TBCs raise the combustion chamber temperature, and one would therefore expect hydrocarbon (HC), carbon monoxide (CO) and soot emissions to be reduced, but NO_x emissions to be increased, since NO_x formation from atmospheric nitrogen becomes critical as temperatures approach 1500°C and above [9]. One explanation advanced has been that, although TBCs increase the average combustion chamber temperature, they decrease the peak temperature, and so reduce NO_x emissions [10].

Catalytic combustion can allow lower combustion temperatures, and has been advocated as a means for reducing NO_x emissions from industrial heat generating furnaces and gas turbine combustors [9]. If it should happen that zirconia-based TBCs promote (or can be modified to promote) some degree of catalytic combustion in the diesel combustion process, this might be an alternate approach for reducing NO_x pollutants from diesel engines.

The present report describes the catalytic combustion of propane in air over bisque-fired m-ZrO_2 doped with three classes of known or potential combustion catalysts: zirconia-stabilizing oxides (CeO_2, Y_2O_3, MgO), transition metal oxides (Co_3O_4, Cr_2O_3, Fe_2O_3), and noble metals (Pt). The investigation was intended as a first step in identifying specific catalytic combustion effects that might be associated, whether for good or bad, with the use of zirconia-based thermal barrier coatings, or possibly other coatings, in diesel engines.

1.1. Catalytic combustion

Propane was chosen as the fuel for our catalytic combustion study because propane is a well-characterized fuel which is recognized in combustion science as being the lightest straight-chain hydrocarbon whose oxidation reactions are typical of higher molecular weight hydrocarbon fuels [11]. In the combustion of propane in air, the overall reaction is:

$$C_3H_8 + O_2 + E_{act.} \rightarrow \text{reactive intermediates, esp. free radicals} \rightarrow \text{branched-chain reaction} \quad (1)$$

where for homogenous gaseous combustion, an activation energy, $E_{act.}$, of about 25-50 Kcal/mole is required [12]. The combustion mixture must be heated therefore for reaction (1) to proceed, with the spontaneous ignition temperature for propane in air being given as 493°C, although this depends on conditions and is not a true constant [13].

Note that the combustion of even a simple gas such as propane in reaction (1) is actually very complex, and may involve as many as 100 intermediate species (including especially free radicals) and 2000 interrelated reactions [14]. Note also that combustion is possible only when a branching chain reaction is sustained within the propane/air mixture. When a catalytic surface is present, the activation energy for reaction (1) is lowered to as little as 11-15 Kcal/mole [12], and saturated hydrocarbons such as C_3H_8 can be ignited in air over Pt catalysts at temperatures as low as 225°C [15].

Catalytic combustion is a mature science which has been the subject of several reviews [9,15-18], and detailed analyses of catalytic combustion mechanisms have been made. The essential elements of catalytic combustion, for the purposes of discussion in the present report, are depicted in Fig. 1.

At temperatures below the catalytic ignition temperature (T_{cat}), no reaction occurs, even though propane ($CH_3CH_2CH_3$ or C_3H_8) has transported through the gas boundary layer, and is co-adsorbed with oxygen on the catalytic surface. When T becomes equal to T_{cat} (i.e., when the activation energy
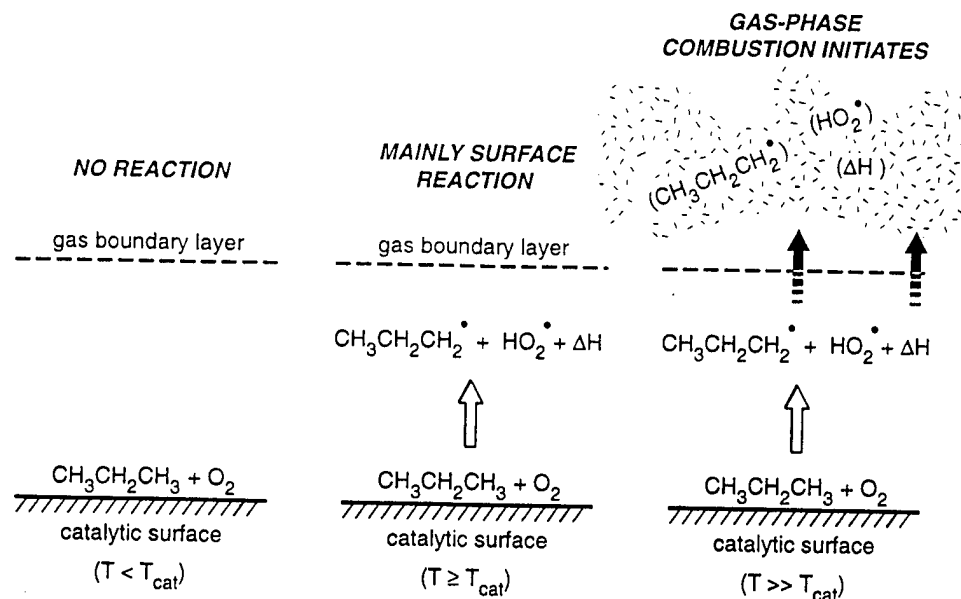
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Figure 1 Regimes of surface catalytic combustion as a function of surface temperature.

necessary for catalytic surface combustion becomes available), reaction commences on the catalytic surface. With Pt, the activation energy is 11-15 Kcal/mol, and T_{cat} is low, being of the order of 200°C. Other combustion catalysts generally exhibit higher T_{cat} values, presumably because they require correspondingly larger activation energies. Once commenced, the catalytic combustion reaction produces highly reactive free radical intermediates such as $CH_3CH_2CH_2^\bullet$ and $HO_2^\bullet$ [14], as well as heat (ΔH), on the surface and within the boundary layer above the catalytic surface. As the temperature becomes still higher, i.e., $T >> T_{cat}$, the reactive intermediates and heat generated at the catalytic surface may pass through the gas boundary layer and act to initiate and stabilize homogeneous gas-phase combustion within the bulk gas [17]. Under certain conditions, this can lead to catalytically stabilized thermal (CST) combustion [17].

In the general case, the homogeneous gas-phase combustion may be sustained, or not sustained, depending primarily upon 1) the ability of the catalyst to remain active at high temperature and 2) the overall fuel/air composition and gas transport/mixing conditions just at the catalytic surface, as well as the heat flow balance within the furnace or engine system itself. It should be recognized, however, that even slight or transitory catalytic combustion reactions could have significant effect in the diesel combustion process.

1.2. Catalytic combustion in internal combustion engines

The literature contains relatively few references which specifically address catalytic reactions occurring during engine combustion. These basically involve studies examining the effect of platinum

or copper, cerium or CeO_2, yttria-stabilized zirconia (either plain or augmented with Pt or Ce), or aluminosilicates. A number of papers deal with smoke suppression or soot oxidation by fuel additives, and several of these are discussed briefly in relationship to catalytic combustion.

1.2.1. Catalytic combustion by metals in IC engines

Before considering platinum catalysts in engines, one should be aware that the catalytic combustion activity of platinum is a problem when Pt or Pt alloy thermocouples are used for temperature mapping of flames. Burton et al [19] have shown, for example, that catalytic combustion at the platinum surface can cause the indicated TC temperatures to be as much as 500°C too high in the preflame and luminous zones of the flame where unburned fuel exists, unless the thermocouple is given a noncatalytic coating. Coatings of SiO_2, $BeO-Y_2O_3$, or $Al_2O_3-K_2SiO_3$ [19] have been used to render the Pt surface noncatalytic.

Also, it is accepted in hobbyist automotive circles that platinum-tipped spark plugs, because of the catalytic activity of Pt, can cause preignition problems in alcohol-fueled racing engines, despite the small Pt surface area and high revolutions/minute of the engine [20]. On the other hand, Pt sparkplugs are thought to be better in the firing of lean gasoline mixtures.

In 1972, Haskell and Legate [21] found that HC emissions from a spark ignition (SI) test engine were <u>increased</u> when an 1/8-in thick Vycor disc, on to which Pt had been vacuum deposited, was cemented onto the piston crown (the Vycor disc being meant to keep the Pt coating hot enough to burn off oil deposits). Moreover, they demonstrated catalytic combustion within the engine by showing that the temperature of a Pt-10%Rh thermocouple introduced through the cylinder head decreased rapidly by 300°C when the fuel was switched from unleaded to leaded, i.e., as Pb poisoned the catalytic Pt-Rh surface. (Lead may thus reduce engine-knock by diminishing surface catalytic combustion, as well as by inhibiting preflame gaseous flame-branching reactions [22].). To explain the increased HC output, Haskell and Legate hypothesized that the catalytic activity of the Pt-Vycor disc changed the composition of the gas boundary layer, with the oxidation products, H_2O and CO_2, replacing fuel and O_2, which caused the flame-quench distance to increase, and HC emissions to be higher " --because the increase in quench distance means that the fuel remaining within this (the flame-quench) distance is more easily mixed by turbulence into the exhaust gases."

However, in 1980, Thring [23] explored the use of Pt in the pre-combustion chamber of a modified (compression ratio reduced to 12:1) indirect injection (IDI) diesel engine, and found improvements including low NO_x and HC emissions as well as multi-fuel capability.

Also in 1980, Gaffney et al [24] reported that thin (6000 Å) Pt coatings sputter-deposited onto the piston crown and valve faces reduced soot emissions from a diesel engine, although the coating was lost within 8 hrs of engine operation. The loss of the Pt coating was attributed by Gaffney et al as probably due to poor platinum adhesion caused by surface impurities such as iron oxide and carbon.

In response to the reports by Thring [23], Gaffney et al [24], and Murray [34] (see below) of reduced gaseous and particulate emissions by in-engine Pt catalysts, Siegla and Plee [25] examined emissions from a production-based IDI diesel engine in which the glow plug, pre-chamber wall, piston crown, and exhaust and intake valve faces were sputter-coated with platinum. The after-test Pt surfaces were all found to be soot covered, with no evidence of Pt loss. In general, no difference (beyond normal standard deviation) was seen in emissions, and Siegla and Plee concluded that Pt coatings provide no significant improvement in emissions of particulate matter, unburned HC, CO or NO_x from a modern, properly-combusting diesel engine. Examination of their data (Fig. 5) suggests, however, that NO_x may have in fact been reduced by 2-7%, with best improvement coming at high engine loads. The effect of Pt coatings on engine power output or fuel economy was not studied.

Catalytic combustion by platinum and palladium coatings on the glow plug in a direct injection diesel has been studied by Mitchell et al [26] as a means for facilitating the burning of methanol in diesel engines. The combustion process was affected by the presence of the coatings, with palladium yielding the greatest reduction in ignition delay and highest percent of premixed burning. Glow plug temperatures were reduced by 100°C for Pt and 150°C for Pd, while still maintaining satisfactory methanol combustion. Brake specific fuel consumption (BSFC) was little affected, being perhaps slightly higher at low power but slightly lower at high power for Pt and Pd. Both coatings provided lower aldehyde emissions, and Pd reduced NO_x emissions as well; however, unburned methanol was increased for both Pt and Pd.

Hu and Ladommatos [27] have recently reported that unburned HC emissions were reduced by 20% by the deposition of a catalytic Pt-Rh coating on the top and side surfaces of the piston crown in an SI laboratory engine. Interestingly, when the Pt-Rh piston crown coating was machined off, leaving Pt-Rh only in the piston-cylinder wall crevice area, a greater reduction in HC emissions was obtained. This was explained by noting that the burned-gas temperature in the expansion and exhaust process was lower when the piston crown was fully Pt-Rh coated (presumably because of additional combustion effects by the piston-top Pt), and that this lower temperature may have resulted in less post-flame oxidation of unburned hydrocarbons, and therefore higher HC emissions than when only the piston crevice area was Pt-Rh coated.

Another metal, copper, has been shown also to have catalytic combustion activity in SI engines. Rychter et al [28] demonstrated that copper wire coils in a prechamber flame ignition device acted to stabilize ignition and combustion in a lean-burn SI engine. Separate tests with a single compression machine (SCM) indicated that Pt worked similarly, and was more effective than Cu, although of course more expensive. The catalyst was said to give "chemical activation of the charge" prior to ignition which facilitates ignition, shortens ignition delay, and strengthens the flame kernel in its initial development phase. A significant extension of the lean misfire limit, and reduction of cycle-to-cycle variations in combustion chamber pressures was observed.

Dhandapani et al [29] have found as well that a copper coating on the piston crown gave improved combustion stability and reduced HC emissions in a lean-burn SI engine, but that the copper coating had little effect on unburned HC emissions when a high-energy ignition system was employed, i.e., when good initial combustion was obtained.

Platinum and copper have therefore shown distinct catalytic combustion effects in IC engines, although the number of tests reported is small, and the results have not always appeared to be beneficial.

1.2.2. Catalytic combustion by oxides in IC engines

In 1925, it was reported that a CeO_2 coating, when applied to the internal cylinder head of gasoline engines, gave a catalytic action which speeded combustion and reduced engine knock [30]. The coating was said also to allow leaner gasoline-air mixtures and to reduce the needs for external cooling. Moreover, one coating application was claimed to have lasted 15,000 miles, while still remaining effective. Tetraethyl lead was introduced as an anti-knock gasoline additive at about this time, however, and this presumably reduced motivation for further development of the CeO_2 catalytic coating.

In 1960, a brief and unascribed news highlight appeared in a trade journal that described test results in which CeO_2 and other "oxygen-deficient MO_2" coatings were claimed to speed up fuel-burning rates, reduce HC emissions, and decrease carbon and varnish deposit formation, in gasoline and diesel engines [31]. The subsequent outcome of this work is not known, however. Little else is readily found in the literature concerning CeO_2 as an in-cylinder combustion catalyst, although Ce is well known as a component in exhaust catalytic converters, and as a fuel additive for smoke suppression and for exhaust particulate trap soot incineration (see below).

In 1994, an investigation was made of the effect of piston surface composition -- aluminum, air-gapped stainless steel, and air-gapped stainless steel with both unsealed and sealed yttria-stabilized zirconia (YSZ) coatings -- on the performance and emissions of a methanol-fueled, direct injection, stratified charge (DISC) engine [32]. The unsealed YSZ gave maximum unburned HC emissions but lowest NO_x, while air-gapped stainless steel yielded lowest HC emissions, but higher NO_x. However, the calculated in-cylinder temperature was highest for unsealed YSZ, followed by sealed YSZ, air-gapped stainless steel, and aluminum, respectively. Given that NO_x normally increases, and unburned HC decreases, with combustion temperature, this implies either that the crown surface temperatures fall in different order to the gas temperatures, or perhaps that the crown surfaces are giving different catalytic combustion effects. Sealing of the YSZ coating reduced HC emissions, which supports the idea that fuel may be trapped in porous TBCs, and then released later in the expansion/exhaust stroke (see below). Little difference in brake thermal efficiency (BTE) was seen for the four piston surfaces, although the authors note that unsealed YSZ may have slightly improved BTE at 1800 rpm and high loads. Temperature-sensitive, screw-in metal microprobes indicated the surface temperature of the air-gapped stainless steel piston crown to range from 540°-720°C. Since modern catalytic converters operate at 600°-700°C, this suggests that temperature, per se, might not be a problem for in-cylinder catalysis.

Refractory oxides such as CeO_2 or Y_2O_3-ZrO_2 are proposed to have advantages over noble metals (Pt) and transition metal oxides in long-term catalytic stability at high temperature, and in the ability to "burn off" carbonaceous deposits and catalyst poisons (e.g., lead oxide) [17]. With regard to engines, properly prepared YSZ thermal barrier coatings have been reported to withstand 14,000 hours of tow-boat diesel engine life; however, except for the exhaust valve faces, all of the YSZ coated surfaces were covered with deposits which contained carbon and calcium sulfate (from fuel S and Ca-additives in the lube oil) [33]. Whether a catalytically-treated TBC could retain combustion catalyst activity under such conditions is uncertain. On the other hand, if the outer surface of the catalyst can be made to operate at 600-750°C, then the catalyst might presumably remain active, just as in catalytic converters, in clean-running engines.

1.2.3. Catalytic combustion by Pt- or Ce-deposited YSZ thermal barrier coatings

In a 1980 study, Murray [34] applied platinum or cerium to yttria-stabilized zirconia (YSZ) thermal barrier coatings, and compared the effects of uncoated, TBC-coated, or TBC + Pt or Ce-coated engine components on power, fuel economy, and emissions. A laboratory engine adaptable for either spark ignition or compression ignition (CI) operation was used at two different compression ratios (CR)

each, i.e., 6:1 and 10:1 for SI, and 14:1 and 18:1 for CI. The air-to-fuel ratio (A-F) was also varied from 14-1 to 18-1, and from 19-1 to 34-1, in the SI and CI engines, respectively.

Both the compression ratio and air-to-fuel ratio were found to be important, and they acted, in several instances, to reverse the order of performance. However, in the SI engine at a CR of 6:1 and A-F of 14-1, the application of Pt and Ce to the TBC decreased engine power by ~10%, increased fuel consumption by ~10%, and gave significantly higher levels of HC and CO, but much lower levels of NO_x emissions. The ignition delay was increased, as well, by Pt (8°) and Ce (4°) as compared to the TBC alone (1°). Murray concluded that, in general, his results indicated that Ce and Pt inhibited combustion and reduced engine performance in the SI engine.

In the CI diesel engine, Pt and Ce again reduced power and increased fuel consumption (especially Ce), and failed to show any advantage, except in the 14:1 CR tests, where NO_x emissions were reduced by 900%. However, this large reduction in NO_x may have been only the result of the lower combustion temperatures that are produced when the combustion process is degraded by the presence of the Pt or Ce coatings.

The application of Pt or Ce catalysts to a TBC surface has therefore given only generally negative results in both SI and CI engines in the investigation by Murray. Two points may be made, however. First, the combustion in Murray's engine may have been unusual, since he comments that maximum brake torque (MBT) could not be reached in many of the CI tests with even 53 degrees advance in the injection timing. Normally, MBT occurs in direct injection diesel engines, such as Murray's configuration, at about 15-20° advance in injection timing [35]. Second, although deleterious, catalytic combustion in internal combustion engines appears to have been clearly observed; that is, the mere application of a thin deposit of Pt or Ce on the TBC surface produced drastic changes in both the SI and CI combustion behavior, and by a mechanism which presumably could have been only catalytic.

1.2.4. In-cylinder, but non-combustion, catalysis in IC engines

A non-combustion catalytic effect has been proposed for aluminosilicate coatings patented for diesel engine use [36]. These coatings are postulated to give an in-cylinder, pre-combustion catalytic action (akin to the catalytic treatment of crude oils in the oil-refining industry) that converts unsaturated components of the diesel fuel to saturated compounds which resist polymerization (i.e., gumming). According to patent claims, the aluminosilicate coating produces reduced gumming, more rapid "chemical preparation of the fuel for ignition" with a resultant reduction in ignition delay,

improved fuel economy, and easier cold weather starting. The aluminosilicate coatings were applied over a molybdenum subcoat which was thought itself to enhance catalysis, either by fuel contact through open porosity (8-12%) in the aluminosilicate layer, or by a promoting action of small amounts (0.002%) of Mo on the aluminosilicate catalyst [37]. This may correlate with the observation in laboratory tests by Cotton et al (see below) that molybdenum was second only to barium in smoke suppression efficiency. The claims made for the aluminosilicate coatings have not been widely confirmed, however.

1.3. Catalytic oxidation of smoke and soot

A related issue to catalytic combustion is the use of fuel additives to reduce smoke and soot particle emissions from engines. Proprietary additives containing such metals as barium or manganese have been employed for many years for smoke reduction [38]. The suppression of soot emission from propane-oxygen diffusion flames by 40 different metals was investigated by Cotton et al [39]. At 2100K (1827°C) flame temperatures, barium, molybdenum, strontium and tungsten were substantially superior to the other metals (including Mn, Cr, Co, Fe, Ce and Y). However, limited tests with lower temperature flames indicated that, at 1900K (1627°C), manganese and iron began to approach barium in smoke suppression effectiveness.

The alkali metals, barium and strontium, suppressed smoke formation even in fuel-rich combustion, whereas the other metal additives (except for Mo and W which gave intermediate behavior) were effective only under oxygen-rich conditions. Cotton et al proposed therefore that two different mechanisms were involved. Barium and the alkali metals were considered to act by increasing the hydroxyl radial content of the combustion environment, with the soot then being oxidized by the reaction: $C_{solid} + OH \rightarrow CO + 1/2\,H_2$. The other metals were thought to act by a different route, with three possible, but unproven mechanisms being suggested, namely: 1) the metal is incorporated in the soot particle and promotes its oxidation; 2) the metal is oxidized, with the oxide then being reduced in a redox reaction with the soot, $M_xO_y + C_{solid} \rightarrow CO + M_xO_{x-1}$; or 3) solid metal oxides are formed, which catalyze the decomposition of water vapor or hydrogen.

Regarding these possible mechanisms, Fenimore and Jones [40] found that manganese was incorporated into the soot particles, and that it lowered the soot oxidation temperature, with the maximum oxidation rate occurring at 680K (407°C) for the catalyzed and at 800K (527°C) for the uncatalyzed soot. Sapziena et al [41] support the third alternative, i.e., that solid metal oxides are formed, but they believe these oxide particles act to promote catalytic combustion rather than the decomposition of water vapor or hydrogen. Metals such as Ce or Y, which form refractory oxides that

are stable under very low oxygen partial pressures, might be especially expected to generate solid oxide microparticles in the combustion chamber. In this connection, it may be noted that Ce and Y were somewhat superior to Mn (although all three were much inferior to Ba) in the 2100K smoke suppression tests by Cotton et al [39].

In what could perhaps be regarded as an extension of smoke suppression, cerium is currently being investigated as a fuel additive intended to facilitate the regeneration of diesel exhaust-system soot particulate traps by lowering the incineration temperature of the collected soot [42,43]. As a fuel additive, cerium provided a lower temperature, and more quasi-continuous, burning of the filter trap soot than either copper or ferrocene [43]. In addition, the cerium fuel additive gave a 20% reduction, presumably because of in-cylinder catalytic oxidation, in raw soot particulate emissions from the engine [43]. An earlier 1000-hr engine test indicated that the cerium fuel additive reduced NO_x emissions and increased engine power, although only slightly (and without conclusive confirmation) in each case [42].

One may speculate that these latter effects could result from catalytic combustion occurring on minute particles of CeO_2 formed by fuel additive burning within the engine cylinder; however, "coating" of the engine cylinder surfaces by CeO_2 probably does not ensue, and such CeO_2 microparticles, if formed, are swept out with the exhaust, since 97% of the fuel additive Ce is collected within the down-stream soot particle trap [43].

This brief review generally supports the idea of catalytic combustion by coatings or surfaces in internal combustion engines. In virtually every case, just a change in the nature of the combustion chamber surfaces has resulted in clearly discernible effects upon the combustion process. These effects, however, appear to have been as often deleterious as they have been beneficial. For catalytic combustion in IC engines to be successful, its deleterious aspects must be minimized, which presumably we can hope to do by study of the interaction between catalytic combustion and the bulk gas-phase process of fuel ignition-and-burning. Also, it is seen that the metals (Pt, Cu) and oxides (CeO_2) which appear to have in-cylinder catalytic combustion activity are also effective (probably not surprisingly) as smoke and soot reduction additives. A study of in-cylinder catalysis by such materials may be beneficial therefore not only in its own right, but as a means for increasing our understanding of how catalytic substances function in smoke/soot suppression, or within catalytic converters.

2. Experimental

A simple, vertically-mounted tube furnace (Fig. 2) was used, which consists of a 23-cm long section of 10-mm ID, 15-mm OD CaO(~5wgt%)-stabilized zirconia tubing (Zr-23, Johnson-Matthey)

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that is wound with resistance-heating wire over a 6.25-cm length at the midsection of the tubing. The premixed propane/air gas stream is introduced through a zirconia tube at the bottom of the furnace, and passes upwards through a 5-cm deep bed of 2-mm zirconia spheres which is contained entirely within the heated zone of the furnace. The temperature of the exiting gas is monitored by a chromel-alumel thermocouple (Model No. KHIN-116(U), Omega Corp.) within a closed-end zirconia tube that rests on the zirconia sphere bed.
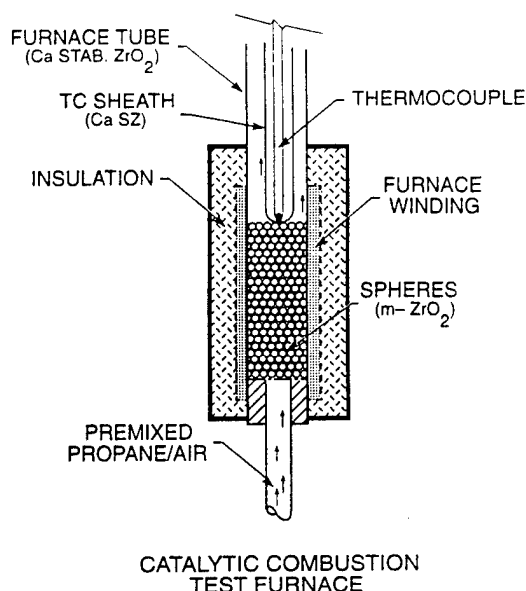

CATALYTIC COMBUSTION
TEST FURNACE

Figure 2 Schematic of the catalytic combustion test furnace.

In the experimental procedure, the flow of a premixed propane/air mixture through the furnace is equilibrated for 5 minutes, and then a selected constant ac voltage of 18 to 24 volts (provided by a variable transformer) is switched to the heating wire. The ensuing rate of gas temperature increase is monitored by computer data acquisition, usually at the rate of 1 reading/second. A plotted comparison of the temperature increase behavior when the gas stream contains a propane/air mixture, as opposed to when it contains only air (with all other factors being kept constant), then allows one to identify any catalytic combustion effects that may be occurring.

The propane was of 99.5% purity (Instrument Purity, Matheson Gas Products), while the air was filtered laboratory supply air. The air flow rate was controlled by an electronic mass flow controller (Model FC-260, Tylan Corp.), and the propane by a precision ball-in-tube flowmeter (Ace Glass Co.). Although a number of flow rates were investigated, the experiments reported here were all conducted using 2.42 l/min of air and 54 ml/min to 325 ml/min of propane, which corresponds to fuel/air equivalence ratios (ϕ) of 0.53 to 3.21. Gas burette measurements verified both flow rates to be accurate to within ±5%. The nominal flow rate through the furnace was ~0.55 meters/sec, with gas velocities within the interstices of the sphere bed being of the order of 3.5 meters/sec. The propane and air were mixed by a junction of 6.35-mm stainless steel tubing, and then passed through a flash arrestor (Model 6103, Matheson Gas Products) before being introduced into the catalytic test furnace.

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The doped ZrO_2 spheres were prepared following the procedures described by Zeng et al [44] using 2-mm bisque-fired monoclinic-ZrO_2 spheres (Zircoa Corp.) and reagent-grade nitrate compounds of the various catalysts (Alfa-Aesar) except for Pt which was used in the form of dihydrogen hexachloroplatinate (Alfa-Aesar). The m-ZrO_2 spheres (6.5 gm samples) were soaked overnight for 16 hrs in 25 ml of 2-molar aqueous solutions of the various catalysts, and then fired for 2 hrs at 700°C in alumina boats before being tested. Soaking for 72 hrs gave no detectible improvement in catalytic performance over the standard 16-hr soaking. X-ray diffraction yielded only an occasional very weak peak indication of the metal oxide dopant, but confirmed that the ZrO_2 remained in the monoclinic form both after firing and after catalytic testing. No analysis of the doped m-ZrO_2 surface or furnace exhaust gas was attempted, since these are not relevant to the purposes of the present investigation.

3. Experimental Results

3.1. Undoped m-ZrO_2 spheres

To determine if m-ZrO_2 itself possesses catalytic combustion activity, control tests were made using undoped m-ZrO_2 spheres which were soaked 16 hrs overnight in water, calcined at 700°C for 2 hrs, and subjected to the standard test procedure. The results are given in Fig. 3, where comparison of Run 1 (propane/air equivalence ratio (ϕ) = 1.4) with Run 2 (ϕ = 0; i.e., pure air) shows an onset of heat release in Run 1 starting at ~750°C. This initial heat release reflects the beginning of combustion catalytic activity on the catalyst surface, which is then followed by breakaway to homogeneous gas-phase combustion commencing at about 840°C.
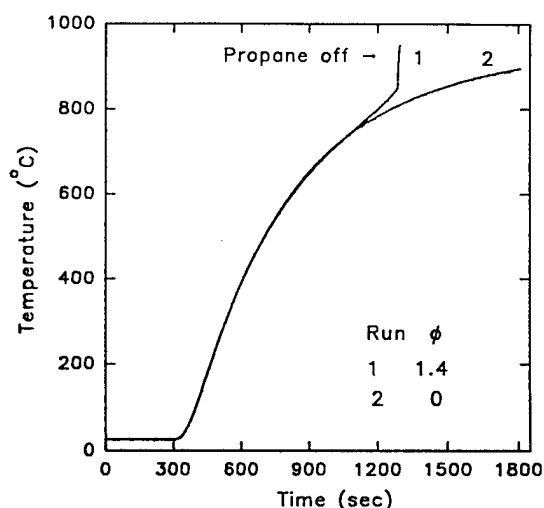

Figure 3 Catalytic combustion behavior of m-ZrO_2 showing onset of catalytic combustion at ~750°C followed by gas-phase combustion at ~840°C.

It is important to note here that, at 750°C, the m-ZrO_2 pellets are beginning to become incandescent, and that all materials tend to show catalytic combustion activity when incandescent [15,17]. Therefore, while the undoped m-ZrO_2 spheres clearly show catalytic combustion activity, it is difficult to say whether this activity results from some unique chemical or physical aspect of the m-ZrO_2 surface, or simply from the fact of the m-ZrO_2 becoming incandescent.

3.2. Pt-doped m-ZrO₂ spheres

When the m-ZrO₂ spheres were Pt-doped, catalytic combustion was detected beginning at about 200°C, as seen by comparing Runs 1-3 (propane/air) with Run 4 (pure air) in Fig. 4. (Note: the individual runs have been displaced along the time-axis in Fig. 4 for clarity). The furnace voltage was switched off at 250°C in Runs 1-3, which allowed the subsequent catalytic combustion behavior to be compared. With ϕ = 1.4 (Run 1), the catalytic combustion was sustained, and the temperature rapidly approached 1000°C before the propane was turned off to avoid overheating the catalyst/furnace system. With ϕ = 1.0 (Run 2), catalytic combustion was also sustained, with an

Figure 4   Combustion over Pt-doped m-ZrO₂ showing ignition at ~200°C and subsequent catalytic combustion behavior as a function of the fuel/air equivalence ratio, ϕ.

apparent equilibrium temperature of about 850°C being obtained. With ϕ = 0.5 (Run 3), catalytic combustion continued up to about 550°C, but then slowly quenched. This is consistent with expected behavior for the given ϕ values, although it must be recognized that achieving sustained combustion is a function of many factors (gas flow rate, rate of heat loss from sphere bed, catalyst stability, etc.) beyond just the fuel/air ratio.
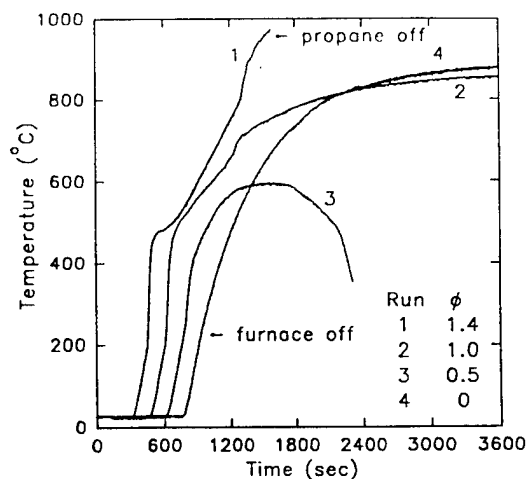
The most significant point to note here, however, is that the results obtained with our simple tube furnace system, especially the 200°C "light-off" temperature, agree well with earlier, more elaborate studies of the combustion of propane/air over platinum [45,46]. This confirms that our tube furnace system provides accurate and meaningful data concerning catalytic combustion.

3.3. Transition metal oxide-doped m-ZrO₂ spheres

Fig. 5 indicates the initiation temperature for catalytic combustion with m-ZrO₂ doped with Cr, Co, and Fe oxides, respectively. In each case, it was the first test of the catalyst, and the fuel/air equivalence ratio was 1.4. The ignition temperatures are approximately 340°C for Cr oxide, 360°C for Co oxide, and 430°C for Fe oxide. These values agree well with the 300-400°C catalytic ignition temperatures found for Cr_2O_3, Co_3O_4 and Fe_2O_3 by Prasad et al [12] in a detailed study of the catalytic combustion of propane using transition metal oxides.

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Except for the higher ignition temperature, the catalytic combustion behavior of the transition metal oxides was essentially the same as for Pt-doped m-ZrO$_2$. Depending upon the fuel/air ratio and aging conditions, instances of "breakaway" homogeneous gas-phase combustion, sustained level 800-900°C catalytic combustion, and non-sustained combustion (just as shown for Pt in Fig. 4) were found with each oxide.

However, the transition metal oxides had a greater tendency than Pt to deactivate with continued testing. This is illustrated in Fig. 6 for Fe$_2$O$_3$ where, despite the propane being turned off at 700°C in Runs 1 and 2 to minimize overheating of the catalyst, the temperature required for the initiation of catalytic combustion increases slightly with each run, although sufficient activity remains in Run 3 to yield sustained catalytic combustion.

Figure 5 Comparison of catalytic combustion ignition temperatures for Cr$_2$O$_3$(340°C), Co$_3$O$_4$(360°C) and Fe$_2$O$_3$(430°C).

3.4. Zirconia stabilizing oxide-doped m-ZrO$_2$ spheres

Typical catalytic combustion behavior for Y$_2$O$_3$-, CeO$_2$- and MgO-doped m-ZrO$_2$ is shown in Fig. 7. Notice that, whereas catalytic combustion initiates with Y$_2$O$_3$ and CeO$_2$ at 550-650°C, there is no evidence of a catalytic combustion effect by MgO, with combustion beginning only at above 800°C (i.e., in the temperature range where "incandescent" catalytic effects come into play.) The lack of catalytic activity by MgO is consistent with the results of Prasad et al [12] who list MgO as being catalytically inert. It may also relate to the
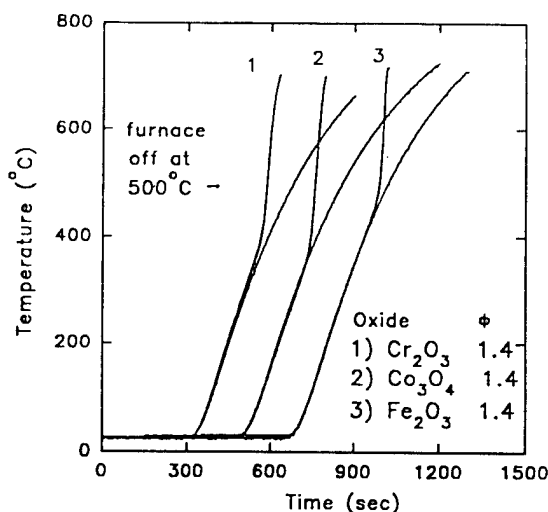

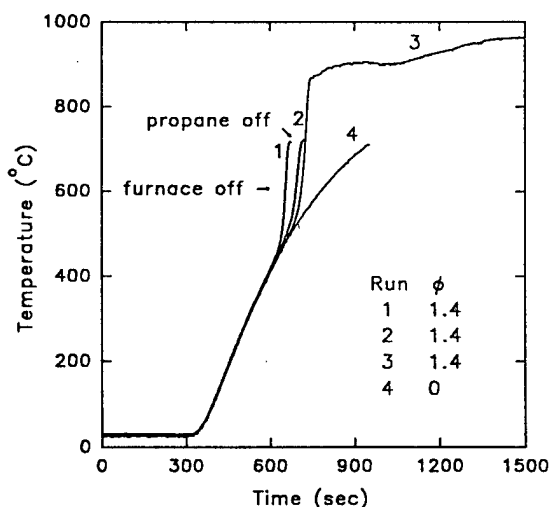**Figure 6** Catalytic combustion by Fe$_2$O$_3$-doped m-ZrO$_2$ showing progressive loss of activity with each experimental test.

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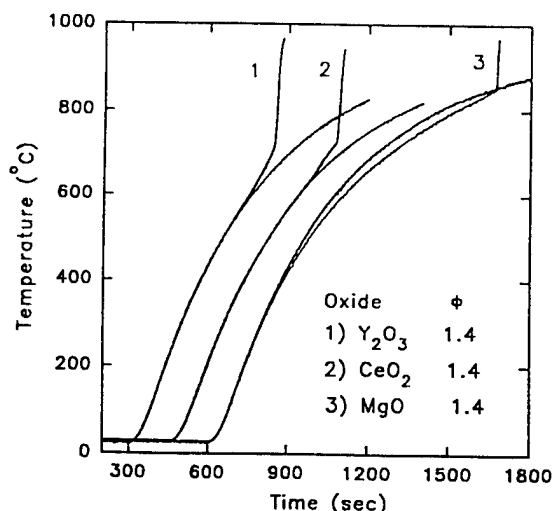fact that Mg(OH)$_2$ is commonly used as a flame retardant.

Figure 7 Comparison of catalytic combustion ignition temperatures for Y$_2$O$_3$(550°C), CeO$_2$(600°C) and MgO (no catalytic activity).
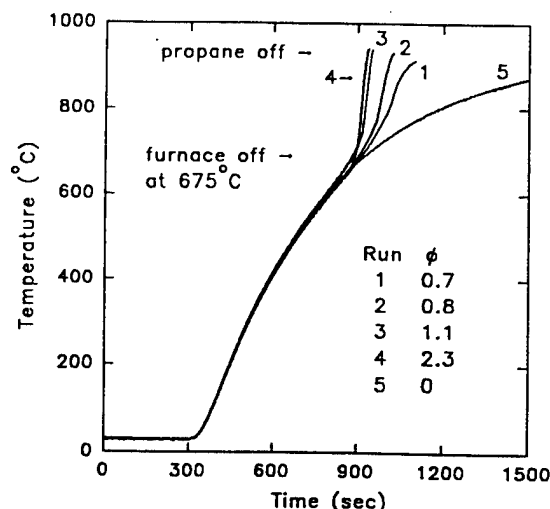
Figure 8 Catalytic combustion behavior of CeO$_2$ showing stability of ignition at 600-650°C for different fuel/air equivalence ratios, ϕ.

Although Y$_2$O$_3$ and CeO$_2$ require higher temperatures for the initiation of catalytic combustion, they may possibly have superior high temperature catalytic stability. This is illustrated in Fig. 8 for CeO$_2$-doped ZrO$_2$ where, for several repeat runs using different fuel/air equivalence ratios, catalytic combustion continues to initiate within the usual 600-650°C temperature range. Oxides such as Y$_2$O$_3$, CeO$_2$ and ZrO$_2$ may therefore be capable of retaining catalytic combustion activity at relatively high temperatures.

4. Discussion

While our results here are for propane, the effectiveness of catalytic combustion in burning petroleum oils is well-documented. The reviews of catalytic combustion [9,15-18] list numerous studies where successful catalytic combustion of diesel fuel, and even #6 fuel oil, was achieved. It seems reasonable therefore to discuss TBC-fitted (or thermally insulated) diesel engine combustion in the context of our present findings.

4.1. Catalytic combustion and the Woschni effect

Woschni and Spindler [7] have found that thermally-insulated engines, when under heavy load, give a higher rate of heat rejection than non-insulated engines. This finding, which appears to contradict common intuition, has received much discussion [8,47], but is still not resolved. The problem has been generally approached from the standpoint of convective heat transfer as described by

$$dq/dt = h_g(T_g - T_w) \qquad (2)$$

where dq/dt is the heat flux, h_g is the gas heat transfer coefficient, and T_g and T_w are the gas and wall temperatures.

Woschni proposes that the anomalously high heat transfer which they observe is caused by a "convection vive" phenomenon [48]. According to Woschni's interpretation, this phenomenon results from the flame burning closer to the wall as the wall surface temperature increases, which causes the laminar boundary layer to be thinned and the temperature gradient immediately at the wall to become steeper, so that the overall effect is to significantly increase the heat transfer coefficient and give greater heat rejection, despite $(T_g - T_w)$ being smaller. This being the case, Woschni concludes that it is impossible to improve fuel consumption by thermal insulation measures.

However in their paper [48], Germerdonk and Nguyen, although they used a premixed propane/air flame with excess air, explain "convection vive" as being caused "--by at least a partial combustion reaction also within the boundary layer at sufficiently elevated wall temperatures." They support this conclusion by an analysis for unburned propane in the boundary layer (their Fig. 10) which shows that propane exists within the boundary layer with little indication of reaction at $T_w = 435°C$, but that the propane within the boundary layer is clearly consumed when $T_w = 768°C$.

This is strong evidence for the role of catalytic combustion in "convection vive," and therefore presumably also in the Woschni engine effect, especially when given that both only begin (cf. Fig. 10 of the Woschni and Spindler publication) after some certain temperature is reached, i.e., the catalytic combustion temperature. In contrast, a thermal/gasdynamic action such as the proposed thinning of the boundary layer would be expected to give only a continuous, smooth change with wall temperature rise, with no abrupt "start/stop" point.

Germerdonk and Nguyen found "convection vive" to begin at about 650°C using a probe test surface they describe only as being a ceramic [48]. This agrees well with the 550-650°C ignition of catalytic combustion observed here with Y_2O_3 and CeO_2 (i.e., "ceramics"). In Woschni's research, high heat rejection began, as shown in their Fig. 10, at about 700K (427°C), which Woschni [8] acknowledges to be lower than the Germerdonk and Nguyen temperature, but proposes nonetheless to result from "convection vive." It is not clear whether Woschni's 700K onset temperature for high heat rejection was determined using a metallic, or a ceramic, probe surface since Woschni and Spindler employed "metal and ceramic disks of different thickness" to vary the probe surface temperature over the range of 400K to 1200K. However, if the outermost surface was metal (Nimonic), then there would be good agreement between the 700K (427°C) "convection vive" onset temperature determined by Woschni and Spindler using a Nimonic (Cr_2O_3-rich surface) probe in a diesel engine, and the ~400°C ignition temperature determined here (Fig. 5), and in the earlier literature [12], for catalytic combustion with transition metal oxides including Cr_2O_3. This latter agreement, if it exists, would be a further indication that the Woschni effect is essentially catalytic combustion, just as with "convection vive."

The possibility of an exothermic reaction in the boundary layer was considered by several discussers of the Woschni effect paper, but the idea was rejected because, as pointed out by Alkidas [8], it is not generally accepted that significant unburned fuel exists in the boundary layer of the cylinder head and liner of a direct injection (DI) diesel engine. This may be true, neglecting residual gases, in the early compression stroke, but perhaps not just before and after TDC of piston travel. For example, it is a recognized problem that discrete quantities of fuel enter porous TBCs and then emerge in a deleterious manner later in the combustion burn, which necessitates sealing of the TBC [5]. Both the cylinder head and piston TBCs are sealed, and if it is truly necessary to seal the cylinder head TBC, this implies that some amount of fuel penetrates the head gas boundary layer even in DI diesel engines. Other authors have expressed concern over fuel being trapped, and later released, in porous plasma sprayed thermal barrier coatings [32,34,49], and even porous carbon combustion chamber deposits [21].

One can also reason indirectly: if "convection vive" is catalytic combustion, as it appears to be; and if the Woschni effect is "convection vive"; then the fact that Woschni's heat probe, situated in the diesel engine head, shows an accelerated heat rejection, only when above some certain temperature, is evidence of fuel in the head gas boundary layer. Indeed, it should be possible, using a heat probe such as Woschni's but one capable of being temperature-controlled and fitted with surfaces of increasing catalytic activity (i.e., Pt, Cr_2O_3, Y_2O_3, etc.), to show unequivocally whether or not fuel occurs in the gas boundary layer at the cylinder head surface.

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Several observations therefore exist to suggest, especially when viewed in the context of our present experimental results, that both "convection vive" and the Woschni high heat rejection effect may be essentially manifestations of catalytic combustion.

4.2. Catalytic combustion role in TBC-fitted engines

However, even if the Woschni effect is catalytic combustion, one must still explain how the combustion problems associated with low heat rejection diesels occur, and what role, if any, that catalytic combustion may have in these problems. The faults commonly identified [4,8,50] for LHR engines are reduced volumetric efficiency, poor fuel/air mixing, faulty ignition delay timing, and the commencement, under high engine loads, of degraded combustion wherein increased fuel consumption, high heat rejection, and the generation of smoke/soot all occur simultaneously.

High temperature alone is probably the essential cause of the reduced volumetric efficiency and poor fuel/air mixing (higher air viscosity and degraded injector performance resulting from the high temperature, high pressure cylinder environment) observed in LHR engines. Catalytic combustion may have an effect, however, in the reduced ignition delay, and possibly also in the later diffusion-controlled burning in the diesel engine cylinder.

When fuel is injected into the diesel engine cylinder, there is a "ignition delay" during which a certain amount of fuel pre-mixes with the engine air, so that combustion consists of two stages: pre-mixed burning and then diffusion-controlled burning as fuel injection continues. The balance is critical, with too much ignition delay producing excessive pre-mixed burning ("diesel knocking"), while too little ignition delay results in low-quality combustion which occurs, on the average, too late in the power stroke, and so reduces engine power and fuel economy.

Thermal barrier coatings, or other thermal insulation, act to shorten the ignition delay and, as generally shown by heat release measurements, to materially reduce the beneficial, early-stage, pre-mixed combustion. In this regard, it should be noted that Sun et al [4] have demonstrated recently that the ignition delay timing problem can be largely remedied, and engine power and fuel economy regained, either by using low-cetane fuel (which by definition lengthens ignition delay) or improved fuel injection rates (more pre-mixing in a given time).

The major effect of TBCs in reducing ignition delay is probably thermal; that is, the combustion chamber is simply hotter which accelerates the diesel ignition process. But a certain degree of catalytic combustion may nonetheless be involved, since TBCs are reported to facilitate the early

starting process of diesel engines [10,51], even though the combustion chamber temperatures are then low. This would be consistent, for example, with the demonstration here of the catalytic combustion activity of Y_2O_3 and possibly even ZrO_2. The effect could, as well, be akin to the ignition advance, i.e., the catalytic "preignition problem," noted earlier for Pt-tipped spark plugs in methanol-fueled engines.

Unfortunately, under engine conditions, it is quite difficult to distinguish between thermal and catalytic fuel ignition effects (except perhaps for cases where known catalysts such as Pt are introduced into the combustion chamber). It remains an important goal to ascertain, however, whether or not catalytic combustion plays a significant role in the reduction of ignition delay by TBCs, for if so, then the remedy would be to seek to reduce the catalytic combustion activity (e.g., perhaps by adding MgO) of the TBC, while maintaining its thermal insulation properties.

A principal deleterious effect of TBCs (or other thermal insulation) may therefore be simply that they elevate the combustion chamber to temperatures at which catalytic combustion on the various surfaces begins to become possible, with such catalytic combustion then acting as an additional source of trouble (beyond just the TBC-induced temperature rise) in maintaining the proper ignition delay timing. As discussed by Pfefferle and Pfefferle [17], most materials tend to become combustion catalytic as the temperature is raised and incandescence is approached, with even "inert" quartz showing catalytic activity at 1170°K [52].

As noted above, it is commonly reported that, although fuel economy and performance may be improved at low load, combustion in TBC-fitted diesel engines becomes degraded when the engine is put under heavy load, with increased fuel consumption, high heat rejection, and smoke/soot generation then occurring simultaneously [8,50]. How these three effects can all occur at the same time has not been fully explained in the literature.

One hypothesis, in answer to this question, would be to suppose that catalytic combustion may be involved, but with two essentially separate effects within the engine. As observed by Sun et al [4], Needham [8], and others, thermal barrier coatings reduce the ignition delay, and as the TBC surface temperature increases under heavy load, catalytic combustion activity on the TBC surface could begin to come into play, resulting in even shorter ignition delay and an especially unfavorable ratio of premixed to diffusion-controlled combustion, i.e., degraded combustion. Then, at some point during the degraded combustion, unburned fuel or fuel vapor may contact the hot TBC surface and undergo "fractionating" catalytic combustion. That is, the lighter molecular weight components of the fuel may be burned on the catalytic surface at relatively moderate temperatures (in the combustion sense) and

so contribute to "high heat rejection", while the heavier components are left unreacted, and result in smoke or soot generation in the engine exhaust. A certain amount of molecular "cracking" may occur as well.

This proposed mechanism for the degradation of combustion by surface catalytic interaction is similar, in many ways, to the flame quenching behaviors already described for catalysts in engines. For example, Robben notes, in the Comments Section of Ref. 28, that his experience on the interaction of gas phase combustion with catalytic surfaces has been that the catalyst quenches gas phase reactions, mainly by removing fuel from the boundary layer. The results of Haskell and Legate [21], Murray [34], Hu and Ladommatos [27], and others also indicate that burning of fuel at the catalytic surface may compromise combustion at the gas-phase flame front, and so degrade overall fuel combustion within the cylinder. This would be especially true if the lighter, more ignitible fuel components were preferentially consumed at the gas boundary/catalytic surface interface. In addition to fuel burning, recombination of reactive flame species (such as free radicals) may occur on the catalytic surface, which would also act to quench gas-phase combustion. The resulting inhibited gas-phase combustion then gives, as has been commonly seen, increased unburned HC emissions accompanied by, because of the lower combustion temperature, reduced NO_x emissions (up to 900% [34]). A similar hypothesis could be made for engines thermally-insulated by other means than TBCs, but with different catalytic surfaces involved, e.g., Cr_2O_3, etc.

At least two arguments might be raised, however, against this proposed explanation of engine catalyst effects. First, fuel is believed to be trapped within porous TBCs, and then released to burn later in the combustion cycle [5]. To support our present hypothesis, one must presume that, in this case, the TBC temperature is too low for catalytic combustion, at the given time or location in the engine cylinder, which allows the fuel to be entrapped/released in the unburned state. Second, Alkidas [53] has shown that an air-gap-insulated, uncooled DI engine could be changed from "thermal-insulation degraded performance" to give superior fuel economy, power, and reduced smoke under heavy load simply by improving engine combustion via increased air usage and injector modification to give better fuel-air mixing. Since the thermal-insulation, and thus combustion chamber temperatures (and surfaces) were not changed, one might ask why the supposed deleterious catalytic combustion should not be seen also with the modified Alkidas engine. However, catalytic combustion is possible only when unburned fuel contacts the catalytic surface, and therefore it should be expected that any improvement in overall combustion, such as achieved by Alkidas, will tend to minimize or eliminate surface catalytic combustion.

A final difficulty in supporting the hypothesis under consideration is that the proposed "fractionating" catalytic combustion of diesel fuel on zirconia or thermally-insulated substrates has not been demonstrated. This is a matter, however, that should be amenable to proof, or disproof, by experimental investigation.

4.3. Prospects for catalytic combustion in IC engines

For catalytic combustion to occur in an IC engine, unburned fuel or reactive flame mixtures must contact a catalytically active surface, and at temperatures above the catalytic ignition temperature, T_{cat}, for that particular surface. Furthermore, T_{cat} may vary significantly as a function of the specific local fuel composition and fuel/air ratio, as well as with fuel and combustion product mass transport within the gas boundary layer. It is also required that the catalytic surface must retain its activity, and not be degraded or deactivated by impinging fuel, unreacted combustion products (carbonaceous residues, soot), lube oil deposits, or high engine temperatures/pressures. And, although perhaps not totally necessary [17], high surface areas are probably desirable for maximum catalytic combustion activity.

In addition, catalytic combustion is likely to be significant only when the basic combustion process is in some way compromised, and complete combustion is not being achieved in the first instance. This is demonstrated by the observation by Dhandapani et al [29] that a copper coating on the piston crown gave improved combustion in a lean burn SI engine, but that the benefit was lost (and not needed) when a high-energy ignition system giving good initial combustion was employed. Another confirmation of this fact is the finding by Siegla and Plee [25] that Pt coatings had no effect on emissions from a properly combusting, production-type diesel engine, although Pt had improved emissions in less-optimized laboratory engines. In other cases, the catalyst may be stable and working, but yet interact in the overall combustion process to give undesirable results. Such a situation is acutely exemplified by the findings of Murray [34] where Pt and Ce coatings on yttria-stabilized zirconia TBCs, although obviously affecting combustion by catalytic means, gave consistently deleterious effects (reduced engine power, greater fuel consumption, and higher HC but lower NO_x emissions) in both SI and CI engines.

The literature indicates essentially two effects for catalytic surfaces such as Pt in engines. The first effect is beneficial, and consists of aiding in the ignition and early-stage combustion of fuels under difficult conditions such as in lean-burn gasoline SI engines, in methanol-fired DI engines, or in combustion chamber crevices. The second effect, however, can be detrimental, and tends to degrade the overall combustion process; it appears to be the result of a quenching of the gas-phase flame-front

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that occurs because of depletion of fuel (by catalytic burning) from the gas boundary layer, and perhaps also recombination of reactive preflame species at the catalytic surface. Therefore, the essential problem with catalytic combustion in IC engines is to understand its particular effect in each instance, and then to modify the combustion process so as to yield the best total combination of power, fuel economy and pollution control.

Given the daunting requirements, it is not surprising that the development of catalytic combustion in IC engines has not been pursued in the past. However, the approach of populous "third-world" nations to Western living standards will soon place tremendous stresses upon the world's fuel reserves and environmental pollution levels, and even complex and "low-return" measures such as catalytic combustion in IC engines may become justified and acceptable under these new circumstances. Moreover, even if catalytic combustion in IC engines is never applied, recognition of its existence may be important for explaining anomalies in "conventional" IC engine combustion (e.g., as perhaps with the Woschni effect here). Such recognition also emphasizes the continuing need to better understand what happens when the flame front, or an unreacted fuel/air mixture, impinges upon the various combustion chamber wall surfaces, and engages in such competitive, but probably surface-sensitive, interactions as gas-phase flame-quenching, convective gas-to-wall heat transfer, or catalytic surface-induced fuel oxidation or cracking.

The most promising use for catalytic combustion principles in future IC engines is likely to be as localized, carefully placed catalyst surfaces intended to alleviate specific problems in advanced concept engines. For instance, LHR engines fitted with TBCs or other thermal-insulation measures may be benefited by non-catalytic "top" coatings (MgO, SiO_2, etc.) which reduce catalytic combustion on combustion chamber surfaces. Other examples might include the use of catalytically active metal or oxide coatings for such purposes as promoting HC and CO oxidation in piston-cylinder wall crevices [27], stabilizing ignition in pre-chamber fitted, lean-burn gasoline engines [28], improving combustion in stratified charge engines [32,54], oxidizing HC and CO at the pre-chamber walls in indirect-injection diesel (IDI) engines [55], or alleviating soot generation in high power-density, "stoichiometric" diesel engines [56]. A current example of one such effort is the investigation by Englehard Corp. of the feasibility of reducing emissions in certain diesel engines by oxidation catalysts and in-cylinder ceramic coatings [57].

5. Summation and Conclusions

Studies of propane/air combustion over catalyst-doped $m-ZrO_2$ spheres confirmed the temperatures at which various candidate materials for catalytic combustion use in diesel engines

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became catalytically active; these being, ~200°C for platinum (noble metals), 360-430°C for Cr_2O_3, Co_3O_4 and Fe_2O_3 (transition metal oxides), and 550-650°C for Y_2O_3 and CeO_2 (ZrO_2 stabilizing oxides). Bisque-fired m-ZrO_2 itself showed combustion catalytic activity, but at ~750°C (i.e., near incandescence where many materials become combustion catalytic). However, MgO inhibited combustion to above 800°C, which suggests MgO coatings as a means for reducing deleterious catalytic combustion in engines.

Comparison of these results with the Woschni phenomenon in thermally-insulated diesel engines indicates that the controversial Woschni effect is in fact catalytic combustion, on the basis: 1) that Woschni and Spindler [7] found high heat transfer to begin, at a (probably) Nimonic Cr_2O_3-rich surface, only above 700K (427°C) surface temperature, i.e. about the catalytic combustion temperature for transition metal oxides; and 2) that "convection vive," a related phenomenon in furnaces [48], was found to begin for a ceramic surface at ~650°C, i.e., the catalytic temperature for "ceramic" Y_2O_3 and CeO_2. Moreover, propane was shown [48] to exist unreacted in the boundary layer for T_{wall} = 435°C, but to be consumed at T_{wall} = 768°C where "convection vive" was occurring.

A review of the literature suggests that combustion catalysts such as Pt (and also possibly transition metal oxides, etc.) can have two opposing effects in IC engines. The first effect is beneficial, and consists of aiding in the ignition and early-stage burning of fuels under difficult combustion conditions. The second effect, however, appears to degrade the overall combustion process by accelerated quenching of the gas-phase flame-front because of depletion of fuel (by catalytic burning) from the gas boundary layer, or perhaps also by recombination of reactive preflame species at the catalytic surface.

In general, catalytic combustion appears to have promise for small, but significant, improvements in the performance and emissions output of IC engines. Best results will probably be achieved in advanced concept engines where the combustion cycle, engine chamber configuration, fuel and operating conditions, and surface catalyst or catalytic treatments have all been "inter-designed" so as to maximize the catalytic combustion benefits.

Acknowledgments

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