Homogeneous Chemistry in Lean-Burn Exhaust Mixtures

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The search for catalysts capable of reducing NO_x in the exhaust of internal combustion engines operated in the lean-burn mode is presently focused on copper-exchanged zeolites. Despite intensive study, the mechanism of reduction over these catalysts is not well understood. In this study new complications are revealed. Specifically, it is demonstrated in a typical synthetic exhaust stream (containing hydrocarbons and oxygen) NO is rapidly, and in some cases nearly completely, homogeneously (no catalyst present) converted to NO_2. Under some conditions N_2O is also formed. It is also shown that most of the hydrocarbons are homogeneously oxidized in these same streams in the temperature range in which lean-burn catalysts are expected to operate. These processes only take place in gas mixtures containing both hydrocarbons and oxygen. Moreover, the extent of NO conversion to NO_2 is shown to be a function of temperature, the hydrocarbon to NO ratio of the input stream, the input CO concentration, and flow rate. In short, homogeneous chemistry is in some cases a significant factor in catalytic NO_x reduction.

Introduction

One of the major efforts in catalysis research for the past decade has been the search for catalysts capable of reducing NO_x in the exhaust of internal combustion engines run in the lean burn mode. For a number of reasons, including efficiency, and a net reduction of undesirable emissions, many engine manufacturers are considering lean burn engines. Unfortunately, supported metal catalysts, (e.g. PtRh/Corderite) presently used as three way catalysts for engines run stoichiometrically are not effective in reducing NO_x in the exhaust produced from lean-burn engines. It is generally agreed that excess oxygen in the exhaust of lean burn engines poisons the active metal sites of these catalysts.[1]

Metal exchanged zeolites, particularly copper exchanged zeolites, are the most intensively studied alternative to present day catalysts. Cu−ZSM-5 and related zeolite catalysts, first introduced by Iwamoto and co-workers,[2−4] are known to reduce substantial fractions of NO_x species carried in exhaust streams. However, these materials loose activity in the presence of oxygen and steam, the activity loss being severe when NO is present in parts per million (PPM) concentrations, typically the case in vehicle exhaust.[5] The latter finding initially suggested that such catalysts are not suited for use in reducing emissions from lean-burn engines. However, an important discovery was made by several groups; when the exhaust contains low concentrations of hydrocarbons, zeolite based catalysts are effective in reducing NO_x, even when oxygen is present in relatively high concentration.[5−8] In fact, tests of Cu-exchanged zeolite catalysts in the presence of synthetic exhaust mixtures containing low concentrations of hydrocarbon show that these materials are moderately effective for NO_x reduction over a broad temperature range.[9,10] Yet, improvements in activity and stability will be required before zeolite based catalysts can be considered for practical application.

Extensive efforts at improving zeolite catalysts have yielded scant performance enhancement in recent years. More detailed understanding of the mechanism of NO_x reduction in the presence of oxygen and hydrocarbons may provide catalyst designers with the insight required to fabricate improved materials. Recent studies of mechanism have shown that the process is very complex, and certainly not as simple as that taking place when NO_x contained in inert streams is catalytically reduced. Yet, at present there is no agreement even on the basic steps involved in the reduction of NO_x from synthetic exhaust streams.

In this study, new complications are revealed. Specifically, it is demonstrated that if both oxygen and hydrocarbon are present in the gas phase (no catalyst present) NO is rapidly, and in some cases extensively, converted to NO_2, and N_2O is formed. Moreover, most of the hydrocarbons are oxidized in these same streams in the temperature range in which lean burn catalysts are expected to operate. It is shown that NO is converted to NO_2, and N_2O formed, only in gas mixtures containing both hydrocarbons and oxygen, and that the final concentrations of the various nitrogen oxides is a function of temperature, hydrocarbon/NO ratio of the input stream, and flow rate. In fact, these findings are fundamentally consistent with earlier studies of fuel lean mixtures containing hydrocarbons and NO. For example, it was found that NO is converted to NO_2 in air/butane (50 to 600 ppm)/NO (0.01 to 200 ppm) mixtures.[11]

These findings have significant implications for catalyst design. For example, models of catalytic reduction[12,13] of nitrogen oxides in lean burn exhaust which assume only NO is present is significant quantities in the gas phase will need to be reexamined. Even laboratory tests of catalytic performance will require careful attention to the actual gas-phase composition at the position of the catalyst bed within the reactor. Measures of input composition may not be sufficient.

Experimental Section

Reactor. A straight, cylindrical quartz tube (35 cm length, by 1.25 cm in diameter) served as the reactor. It was placed in

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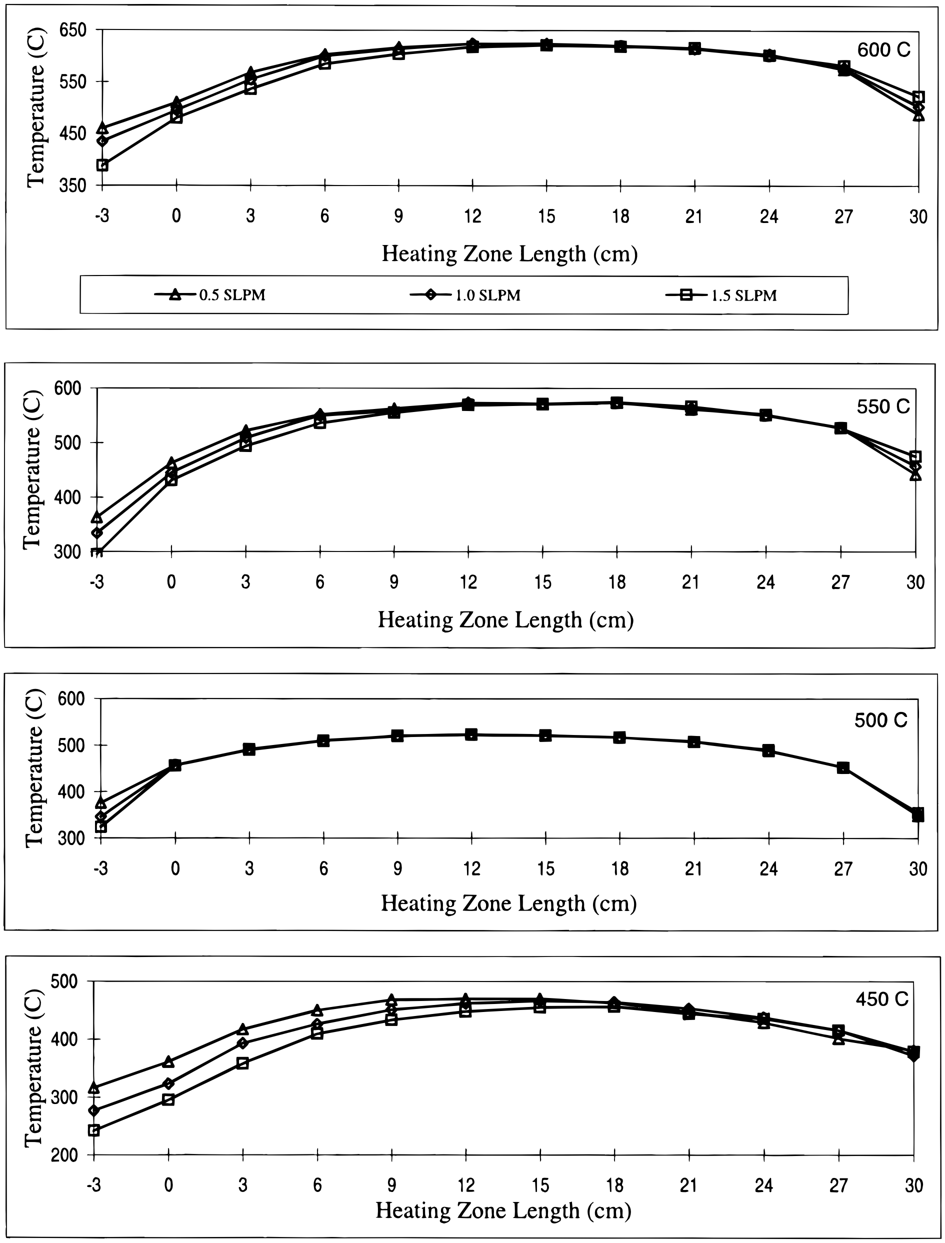

Figure 1. Temperature profiles. The temperature profiles in the quartz reactor with a flowing standard reaction mixture (Table 1) as a function of the nominal temperature and total flow rate at standard temperature and pressure.

a Lindberg/Blue M furnace (Model 55031) with a heating zone of length 30 cm. Both ends of the furnace were enclosed, using ceramic collars which fit snugly around each end of the reactor.

In a reaction controlled by catalytic processes, it is relatively trivial to establish small catalyst beds across which temperature gradients are negligible. In the present instance, the focus is on homogeneous processes and hence temperature throughout the reactor is significant. In Figure 1, temperature profiles in reaction mixtures within the heated zone of the reactor are shown. Clearly, there is a gradient, but along most of this zone the temperature is within 25 °C of the nominal temperature. There is a small impact of flow rate on the profile as well, but it is not significant across the hottest part of the reactor. It should be noted that the profiles are characterized over the same range of flow rates employed in the kinetic studies. In the remainder of this work the nominal temperature is referenced, with the understanding that a temperature gradient existed.

Gas Mixture. Six different premixed gas tanks provided by Scott Specialty Gases or the Los Alamos Gas Facility were used to create a mixture which roughly approximates that found in the exhaust of lean burn engines. The composition of each tank, and the flow under standard conditions, are given in Table 1.

Analysis. Two different analytical instruments were used at the effluent of the reactor to study the composition of the exhaust stream: A Teledyne Model 911 NO_x Analyzer and an MTI Model M200 dual column chromatagraph. The NO_x analyzer provided real-time analysis of the concentrations of both NO and NO_2, but does not detect N_2O. The chromatagraph, containing a 5A Molecular Seive column for the analysis of permanent gases and N_2O, and a PoraPlot Q column provided analysis of the hydrocarbons.

These instruments were placed on parallel exit lines as it was found that the NO_x analyzer, which utilizes ozone to excite NO species, modified the composition of the effluent.

One major concern expressed in previous studies regards the tendency of NO to be converted to NO_2 at low temperatures (ca. 300 K) in the presence of oxygen. Indeed, it was pointed out by Li and Hall[14] that this reaction is thermodynamically favored and at high NO concentrations is likely to occur in the ambient temperature region between the reactor and the analyti-

TABLE 1: "Standard Conditions" Defined as Space Velocity of 25 000/h and an Input NO Concentration of 250 ppm. Standard Input Ratios: (a) Hydrocarbon:NO, 3:1, (b) Propene:Propane, 1:3, (c) CO:NO, 1.5:1

				flow rate (sccm), space velocity 1400/h				
tank	composition	concentration	balance	450 °C	500 °C	550 °C	600 °C	net concentration under standard conditions at all temperatures/pressures/flow rates
1	nitrogen	(100%)		520	480	450	420	70%
2	oxygen	(100%)		59	55	52	48	8%
3	carbon dioxide	(100%)		52	48	45	42	7%
4	propane	2500 ppm	nitrogen	52	49	46	43	700 ppm
	propene	7500 ppm						
5	NO	1.01%	nitrogen	18.7	17.5	16.4	15.3	250 ppm
6	carbon monoxide	7500 ppm	nitrogen	39	37	35	32	400 ppm
	hydrogen	2500 ppm						
	sulfur dioxide	250 ppm						

cal instrumentation. However, these workers also note that for NO concentrations in the ppm range, kinetic limitations should make this conversion inconsequential.[15] To test for this phenomenon, oxygen (8%), NO (300 ppm) and nitrogen (balance) were passed through the usual plumbing (reactor to NO_x analyzer) at ambient temperature (approximately 300 K) and at the lowest flow rate used experimentally (0.3 standard liters per minute). No NO_2 was detected. For this reason, it is believed that all NO and NO_2 readings accurately reflect the concentrations produced in the reactor at high temperature.

Results

NO_2 and N_2O Production. The key results can be seen in Figure 2. It is clear from this figure, that at temperatures above 450 °C in a mixture of both hydrocarbons and oxygen, homogeneous processes can lead to NO concentration decreases, as well as the formation of NO_2 and N_2O. As shown in Table 2 there is no NO_2 or N_2O formation in the absence of either oxygen or hydrocarbons, even at 600 °C. It is later argued that NO_2 is formed primarily (not exclusively) from NO, and N_2O is formed primarily from nitrogen molecules. The figure also reveals the impact of temperature and flow rate on the concentrations of the various nitrogen oxides.

Some results are of particular interest. First, it should be noted that very little NO_2 or N_2O is formed at 450 °C at any flow rate. Indeed, at temperatures below 450 °C only NO was detected in this work. Second, the changes in concentration as a function of flow rate of NO_2 and N_2O suggest rough outlines for the mechanisms of the homogeneous processes. For example, at 600 °C it is clear that the concentration of NO_2 actually shows a maximum and the concentration of NO a corresponding minimum as a function of flow rate. This means that over a broad range of flow rates the NO_2 concentration actually decreases with increasing residence time (decreasing space velocity). These same phenomena are not found at lower temperatures. Also noteworthy at 600 °C is the fact that N_2O is only observed at the highest flow rate employed.

A third important finding is the inverse relationship between the NO and the NO_2 concentrations at all temperatures. The sum of the concentrations of these two species nearly equals the same value in all cases. N_2O concentration, highest at 550 °C, does not appear to correlate to the concentrations of the other two nitrogen oxides.

Figure 3 contains data on the impact of both flow rate and the ratio of hydrocarbons (HC) to NO in the feed stream on the NO_2 production rate at 600 °C. For these plots the total flow rate was held constant by adjusting the nitrogen "balance," as was the temperature and the concentration of all species (including NO), except that of propane and propene. The concentrations of propane and propene (1:3 ratio) were increased moving from left to right on the figures. As shown in both plots, the concentration of NO_2 increases with an increasing HC/NO ratio, and correlates with an opposite trend for NO. This suggests there is little NO conversion in the absence of hydrocarbons. (Indeed, in the complete absence of hydrocarbon there is no conversion of NO.) Also, at any given HC/NO ratio there is more NO_2 as well as more N_2O present at the lower space velocity (bottom chart).

The precise chemistry of the homogeneous process is clearly sensitive to many parameters. Additional evidence can be seen in the impact of increasing the input CO concentration on the concentrations of the nitrogen oxides at 600 °C. As can be seen in Figure 4, increasing the input concentration of CO while keeping all other concentrations constant, and the temperature and total flow rate constant, increases the production of NO_2. Unfortunately, it is not possible to clearly state the impact of CO concentration on NO_2 and N_2O production. As shown below, significant CO is generated due to hydrocarbon combustion, indicating that CO concentration is a strong function of many parameters, including position along the heated zone.

Hydrocarbon Reactions. Additional evidence of the existence of homogeneous reactions can be found in the changing concentrations of hydrocarbons and carbon monoxide. As shown in Figure 5 virtually all of the hydrocarbons are combusted at low flow rates at 600 °C. Even at 500 °C a considerable fraction of the hydrocarbon is combusted at low flow rates. Consistent with simple homogeneous kinetics is the finding that the fraction of hydrocarbon which is combusted increases as the space velocity is reduced (residence time increased). It should be noted that these results are consistent with reports of homogeneous combustion of hydrocarbons in similar lean-burn exhaust mixtures reported by Hall and coworkers.[16]

The concentrations of carbon monoxide in the exit stream at 600 °C are far higher than that in the input (250 ppm) giving additional direct evidence of significant homogeneous processes (Figure 6). There is virtually no difference between input concentration and output concentrations of CO at 500 °C, even at those flow rates where almost half the hydrocarbons have combusted (see Figure 5). This raises the question of the origin of the very high CO concentrations at 600 °C. Is CO formed entirely from hydrocarbon combustion? The impact of space velocity, on the concentration of carbon monoxide at 600 °C is of interest in this regard. It clearly reaches a maximum at a space velocity between 2500 and 3000/h. This does not correlate to the extent of hydrocarbon combustion.

Discussion

Homogeneous chemistry in lean-burn exhaust mixtures was not thoroughly investigated in most prior studies of lean-burn exhaust catalysis. Yet, the experimental results of the present study, and some other recent studies,[16] demonstrate that homogeneous processes can play a significant role in the chemistry of lean-burn exhaust. These results reinforce the

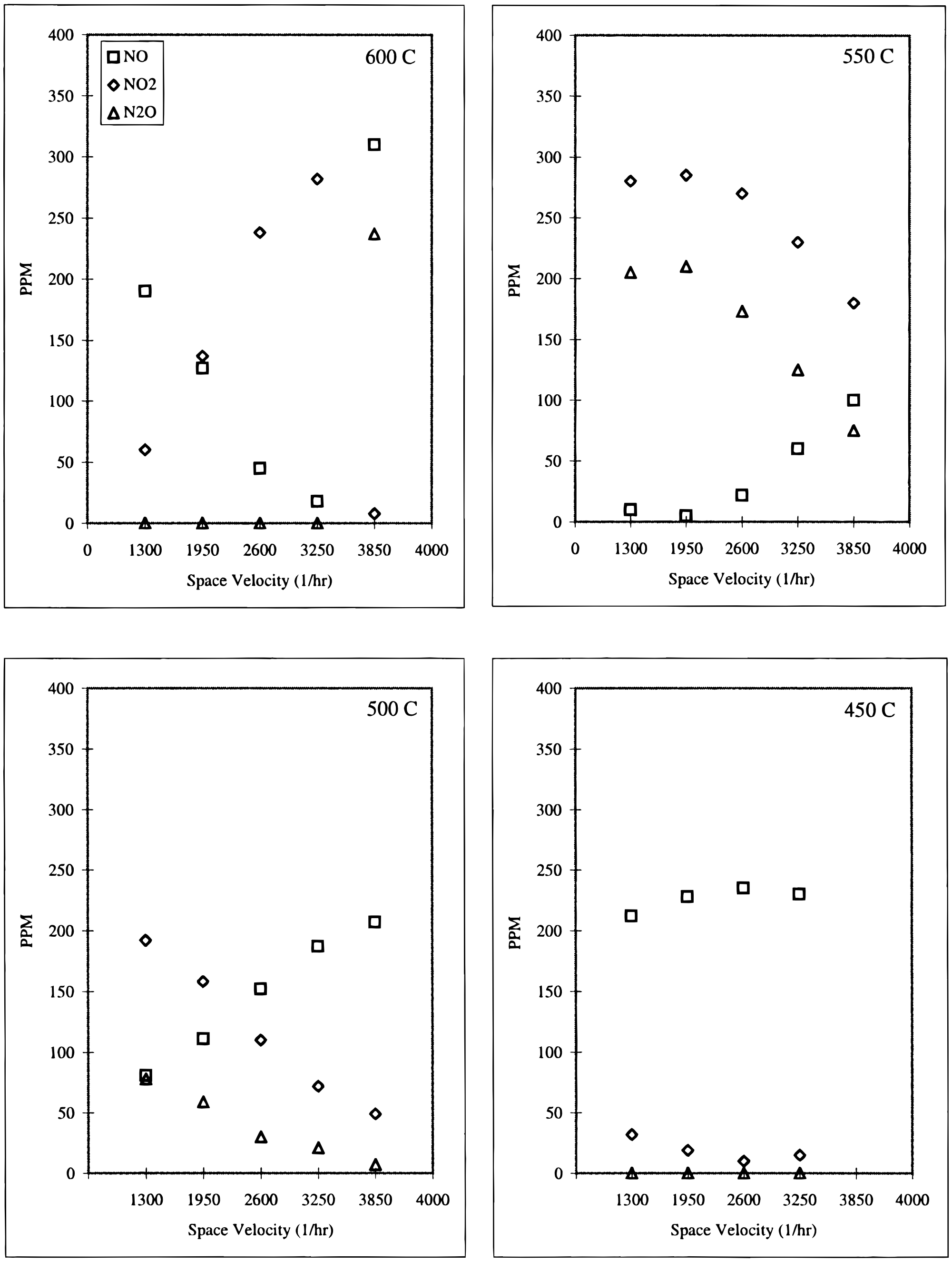

Figure 2. Temperature and flow rate impact on NO_x profiles. Nitrogen oxide concentrations were measured at the reactor oulet. Standard reaction mixture employed in each case.

TABLE 2: NO_x Formation in Incomplete Mixtures (Nitrogen as the Carrier/Balance Gas)

NO, ppm in	hydrocarbons, ppm		oxygen, ppm		space velocity 1/h	NO_2, ppm	
	in	out	in	out		in	out
250	500	500	0	0	800	0	0
250	1000	985	0	0	1200	0	5
250	1500	1500	0	0	1600	0	3
250	0	0	18100	18100	800	0	0
250	0	0	18200	18200	1200	0	3
250	0	0	18300	18300	1600	0	3

supposition that extensive control studies are a necessary part of all scientific inquiry. The data also indicate the need to consider homogeneous processes in the creation of mechanistic models of the catalytic reduction of NO_x species in lean-burn exhausts.

Many models,[17−19] as well as some experimental work[20,21] suggest that NO_2 is a necessary intermediate for NO_x reduction over zeolite catalysts. The present work and some earlier studies (which employed very different conditions) as well[11,22,23] indicate that in some environments the primary source of NO_2 may be homogeneous, rather than catalytic, processes.

The data from the current study can be used to conjecture about homogeneous processes in lean-burn exhausts at various levels of certainty. At the highest level of certainty the data indicate the following regarding processes taking place above 500 °C: (i) a significant fraction of the NO is removed, (ii) NO_2 is generated, (iii) N_2O is generated, (iv) the hydrocarbons are combusted, and (v) CO is formed. At the next level of certainty, it is conjectured that NO_2 is largely formed from NO. This would account for the fact that the concentrations of the two species are correlated. The sum of the two concentrations nearly equals the input concentration of NO.

It is also highly reasonable to postulate that the hydrocarbons are combusted via thoroughly studied mechanistic routes. Thus,

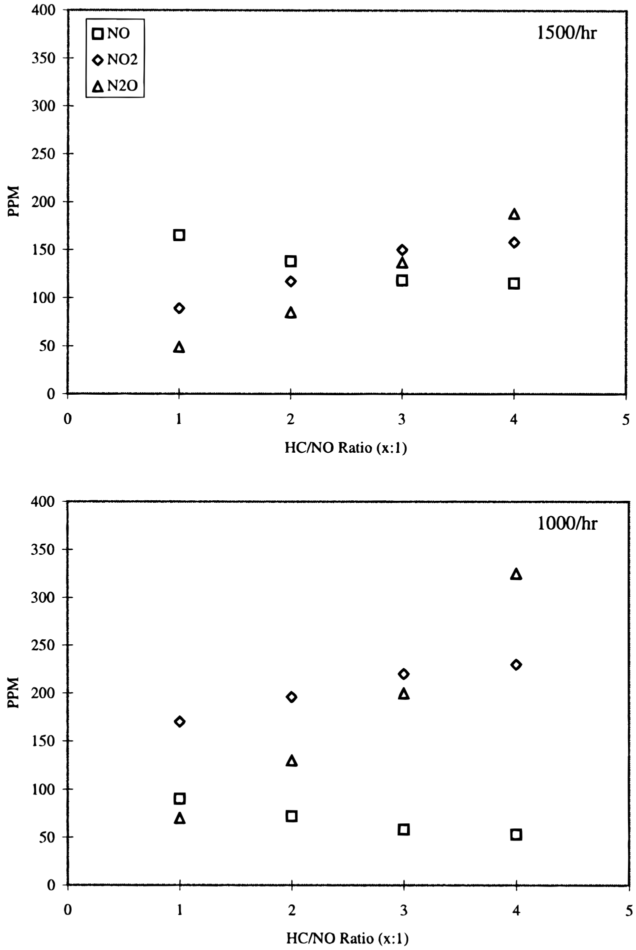

Figure 3. Hydrocarbon impact on NO$_x$ profiles. The impact of changing the ratio of hydrocarbons to NO in the input stream was measured at 600 °C for two different total space velocities.

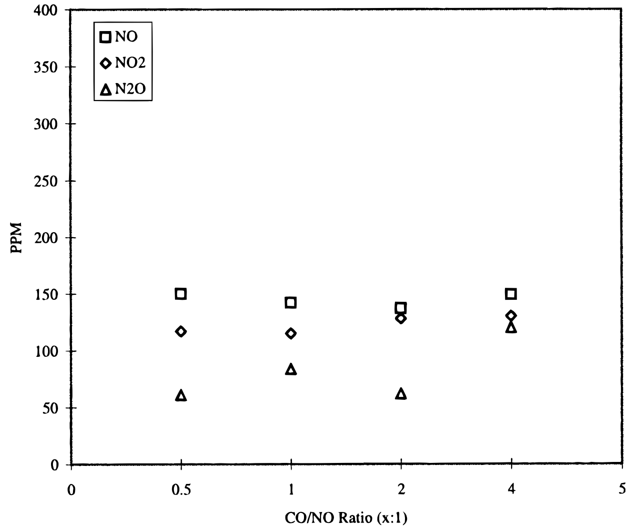

Figure 4. CO impact on NO$_x$ profiles. The impact of changing the ratio of CO to NO in the input stream was measured at 600 °C.

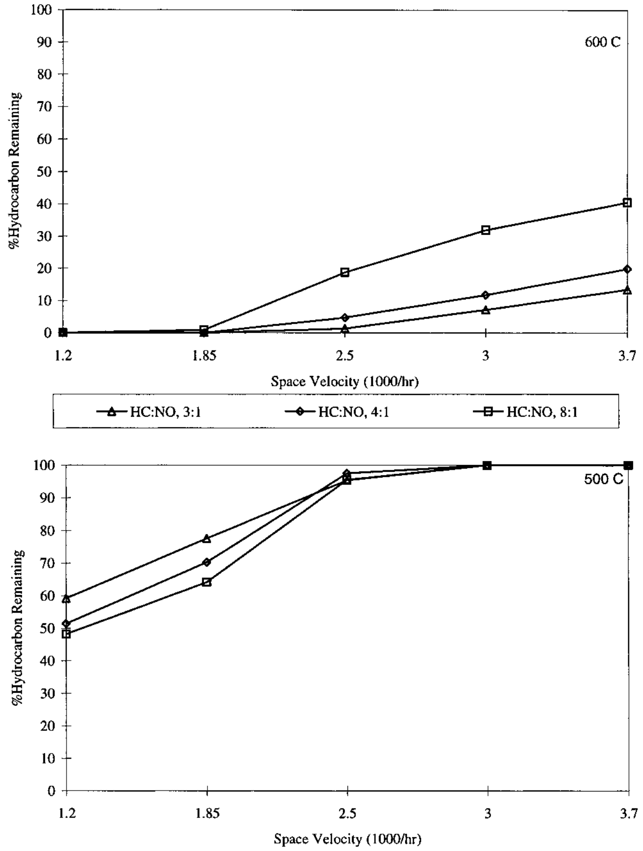

Figure 5. Hydrocarbon combustion. The impact of flow rate (standard mixture, Table 1) on the concentration of remaining hydrocarbons was determined at two temperatures.

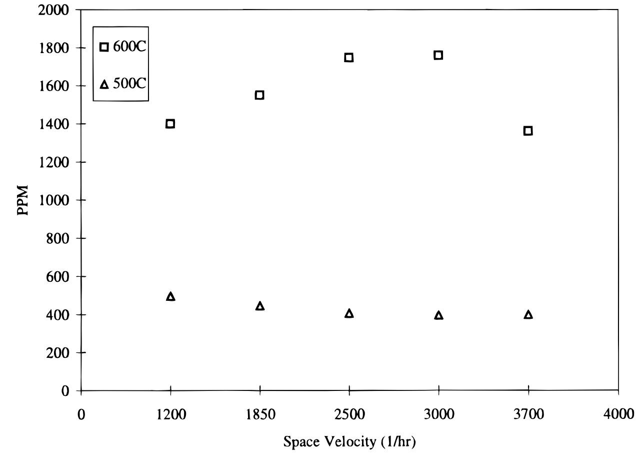

Figure 6. CO concentration at outlet. The impact of temperature (standard mixture, Table 1) on the amount of CO at the reactor outlet was determined at two temperatures.

for example, at the temperatures at which these studies were conducted pentene oxidation is known to take place via a process in which HO_2 is the primary chain carrying radical.[24,25] As shown in Table 3 HO_2 is known to react rapidly with NO to form NO_2. The formation of N_2O can also take place via interactions of N_2 with HO2, although the high concentration found in some instances suggests other radicals may be present as well (Table 3). Indeed, the known mechanisms for hydrocarbon combustion and HOx formation are complex networks of reactions, and it is apparent that many radicals must be present.

A short and partial list of probable reactions significant to the homogeneous chemistry taking place in lean-burn exhaust is given in Table 3. It is clear from this short list that the presentation of even a "qualitative" model of the process is not feasible. A brief review of the literature indicates the network of reactions is far too complex to be understood without extensive computation. Still, even the few reactions listed in Table 3 allow a some understanding of some of the gross scale observations made in the present work.

For example, once the combustion mechanism is considered the observation that NO_2 forms becomes understandable. Under

TABLE 3: Important Reactions in the Transformation of Nitrogen Oxides

reaction	species interactions	reaction rates, $k(T) = A \exp(-E_a/RT)$ A	E_a (cal)	ref
1	$NO + HO_2 \leftrightarrow NO_2 + OH$	2.110E+12[a]	−479	26
2	$NO_2 + H \leftrightarrow NO_2 + OH$	3.500E+14	1500	26
3	$NO_2 + O \leftrightarrow NO_2 + O_2$	1.000E+13	600	26
4	$C_3H_8 + O_2 \leftrightarrow C_3H_7 + HO_2$	1.398E+13	47 500	27
5	$C_3H_6 + O_2 \leftrightarrow C_3H_5 + HO_2$	1.000E+14	38 500	25
6	$C_3H_8 + OH \leftrightarrow C_3H_7 + H_2O$	4.170E+08	850	26
7	$C_3H_7 + HO_2 \leftrightarrow C_3H_7O + OH$	3.240E+13	0	26
8	$N_2O + M \leftrightarrow N_2 + O + M$	1.600E+14	51 600	26
9	$N_2O + H \leftrightarrow N_2 + OH$	7.600E+13	15 200	26

the conditions of the experiment thermodynamics predicts virtually no NO_2 should exist. Indeed, it is well-known both thermodynamically and experimentally that NO_2 cannot be directly formed from NO at the temperatures and pressures at which the work was conducted. A mechanism other than the direct oxidation of NO must be postulated. The first reaction in Table 3 is in fact anticipated, as HO_2 is the dominant radical in the combustion process (e.g. reactions 4−7) at the temperatures employed.

It is also possible to now understand the formation of NO_2 from NO, in apparent violation of thermodynamics. Many combustion processes are known which produce disequilibrium concentrations of some species via complex kinetic processes. This is not a violation of thermodynamics as the system as a whole has the correct thermodynamic "trajectory". The creation of radical species, particularly HO_2 during hydrocarbon combustion provides a kinetic mechanism for NO conversion to NO_2.

The table also suggests means for N_2O to form. In lean-burn mixtures reaction 8 is postulated to be the primary route to N_2O formation and reaction 9 the principle removal reaction.

The tabulated reactions can also explain the odd changes in NO_2 concentration with residence time detected at 600 °C. The second and third reactions in the table are rapid, but depend on high concentrations of radicals other than HO_2. Given sufficient time these concentrations increase and the thermodynamically correct NO to NO_2 ratio will be observed. Specifically, if the residence time is sufficiently long (space velocity sufficiently small) the following sequence will be observed: (i) hydrocarbons combustion leads to HO_2 formation, (ii) NO_2 and N_2O will form, (iii) with increasing residence time other radical concentrations increase (e.g. O, OH, H), thus (iv) the reactions which reconvert NO_2 to NO will dominate. Qualitatively this is consistent with the observation that at 600 °C the concentration of NO_2 actually decreases with increasing residence time (Figure 3).

Summary

The finding that homogeneous processes strongly impact the chemistry of the exhaust stream has important engineering implications. For example, it indicates that the placement of catalytic material relative to the engine exhaust will critically impact not only the catalyst temperature but also the concentration of both hydrocarbons and NO_x species. This in turn will impact the effectiveness of any heterogeneous catalyst. A catalyst close to the engine will operate in the position in the exhaust pipe location at which the highest temperature, highest hydrocarbon concentration, and likely highest NO_2 concentrations are present. A catalyst further from the engine will clearly operate at lower temperature (an advantage for some of the new generation NO_x reduction catalysts), but also a significantly lower hydrocarbon concentration (disadvantage), and probably a lower NO_2 concentration (possible dis/advantage). These results also indicate the need to consider homogeneous processes, including possible roles for homogeneously formed radicals, in mechanistic models of catalytic reduction of NO_x in lean-burn systems.

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