



Kathleen C. Taylor

# Automobile Catalytic Converters

With 23 Figures

Springer-Verlag  
Berlin Heidelberg New York Tokyo 1984

Kathleen C. Taylor

Physical Chemistry Department General Motors Research Laboratories  
Warren, Michigan 48 090, USA

ISBN-13:978-3-540-13064-2 e-ISBN-13:978-3-642-69486-8

DOI: 10.1007/978-3-642-69486-8

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks.

Under § 54 of the German Copyright Law where copies are made for other than private use a fee is payable to 'Verwertungsgesellschaft Wort', Munich.

© Springer-Verlag, Berlin, Heidelberg 1984

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that names are exempt from the relevant protective laws and regulations and therefore free for general use.

2154/3020-543210

## **Preface**

The use of catalytic converters for the purification of automotive exhaust gases is a relatively new technology which was brought into existence by social pressures for the preservation of acceptable environmental conditions. The majority of catalytic practitioners have been able to watch the growth of this technology from its inception to its current state of sophistication. Automotive catalytic converter technology is now in a mature state, and this chapter from Vol. 5 Catalysis: Science and Technology by Dr. K. C. Taylor provides a review which covers both the process chemistry and the most important converter design factors.

# Contents

1. Introduction . . . . .	1
2. Emission Regulations in the United States . . . . .	1
3. Exhaust Emission Characteristics . . . . .	3
4. 1981 Emission Control Technology . . . . .	5
A. Converters . . . . .	5
B. Control System . . . . .	7
5. Catalyst Screening . . . . .	8
6. Laboratory Testing . . . . .	10
7. The Chemical Reactions . . . . .	13
8. Composition of Three-Way Catalysts . . . . .	16
A. Rhodium . . . . .	17
B. Platinum . . . . .	21
C. Palladium . . . . .	22
D. Iridium . . . . .	22
E. Ruthenium and Nickel . . . . .	23
F. Cerium Oxide . . . . .	23
G. Search for Alternatives to Noble Metals . . . . .	24
9. Catalyst Supports . . . . .	25
A. Pellets . . . . .	26
B. Monoliths . . . . .	26
10. The Transient Behavior of Three-Way Catalysts . . . . .	27
11. Deterioration of Three-Way Catalysts . . . . .	35
A. Thermal Effects . . . . .	35
B. Phosphorus Poisoning . . . . .	37
C. Lead Poisoning . . . . .	38
D. Catalyst Poisoning by Sulfur . . . . .	40
12. The 0.4 NO <sub>x</sub> Research Objective . . . . .	41
13. Control of Diesel Particulate Emissions . . . . .	42
14. Exhaust Gas Purification for Europe . . . . .	43
15. Concluding Remarks . . . . .	45
16. References . . . . .	46
Subject Index . . . . .	53

## 1. Introduction

Catalysts have been widely used to lower the emissions of carbon monoxide (CO) and hydrocarbons (HC) in the exhaust of automobiles in the United States since the introduction of 1975 models in the fall of 1974. These catalysts, contained in so-called catalytic converters in the exhaust system of automobiles, promote the oxidation of CO and HC to CO<sub>2</sub> and H<sub>2</sub>O under net oxidizing conditions (*e.g.* A/F > 14.6<sup>1</sup>). Until 1978, emission control requirements for nitrogen oxide (NO<sub>x</sub>) emissions were met through non-catalyst technology, primarily exhaust gas recirculation (EGR) [1, 2]. Starting with some vehicles sold in California in 1977, NO<sub>x</sub> emissions from gasoline engines have been subject to catalytic control. The catalyst here has the additional function to promote the reduction of NO to N<sub>2</sub> via reaction of NO with hydrogen or CO. Catalyst systems designed to reduce NO<sub>x</sub> are considerably more complex than the earlier control systems. For example, the control system introduced by General Motors on some 1978 model year cars has closed-loop air-fuel ratio control (closed-loop fuel metering system, exhaust gas oxygen sensor, and an electronic control unit) as well as a three-way catalyst which simultaneously promotes the conversion of HC, CO, and NO<sub>x</sub> [3]. Stringent federally mandated emission control requirements of 1 gram per mile (g mi<sup>-1</sup>) for NO<sub>x</sub> have led to the further application of three-way catalysts. This review will emphasize the state-of-the-art of catalytic control of automobile exhaust emissions since 1978, specifically three-way catalysts. A recent review by J. Kummer covers part of this period and earlier years [4]. Other reviews of this subject are listed in the reference section [5–14].

## 2. Emission Regulations in the United States

Table 1 lists the passenger car emission control requirements (current as of September, 1982) for all passenger cars sold in the United States except where waivers have been granted by the Environmental Protection Agency for specific vehicles. The law is currently under review (1982) so these requirements may be changed for future years. The 1981 exhaust standards represent a reduction from uncontrolled 1960 levels of 96% for HC, 96% for CO, and 76% for NO<sub>x</sub>.

Exhaust emissions of an automobile are compared with the standard according to a preproduction certification procedure. Certification requires an 80,450 km (50,000 mi) durability test on a prototype car for each engine

---

<sup>1</sup> A/F ≡ air-to-fuel ratio

family, drivetrain, and catalyst combination. The durability mileage is accumulated on an approved route according to a pre-established driving schedule, the AMA cycle. Prior to mileage accumulation and at set mileage intervals during the AMA, emission tests are conducted on the vehicle. The term 1975 Federal Test Procedure (FTP) is commonly used to refer to the emission test (also called CVS-CH test) by which the vehicle emissions are compared with the emission control requirements. The 1975 FTP is a standardized 23 cycle driving schedule for which vehicle preconditioning, driving speed, and test duration are specified. The vehicle is driven on a dynamometer, and the exhaust emissions are sampled and analyzed for HC, CO, and NO<sub>x</sub>. The analysis techniques used are nondispersive infrared for CO, flame ionization for HC, and chemiluminescence for NO<sub>x</sub>. The exhaust emission test results determined according to the 1975 FTP between 8045 and 80,450 km are plotted versus mileage; and the ratio of the least squares estimate of the

**Table 1.** Passenger car regulatory exhaust emission control requirements in the United States. Emissions are expressed in grams per mile (g mi<sup>-1</sup>)

Model Year	1975-76	1977-79	1980	1981-82	1983
HC	1.5	1.5	0.41	0.41	0.41
	CA 0.9 <sup>c</sup>	CA .41	CA 0.39	CA 0.39	CA 0.39
CO	15	15	7.0	3.4 <sup>a</sup>	3.4
	CA 9.0	CA 9.0	CA 9.0	CA Opt. <sup>d</sup>	CA 7.0
NO <sub>x</sub>	3.1	2.0	2.0	1.0 <sup>b</sup>	1.0 <sup>b</sup>
	CA 2.0	CA 1.5	CA 1.0	CA Opt. <sup>d</sup>	CA 0.4

<sup>a</sup> Possible 2 year waiver to 7 g mi<sup>-1</sup>.

<sup>b</sup> Possible waiver to 1.5 g mi<sup>-1</sup> for diesel or innovative technology through 1984.

<sup>c</sup> CA designates California.

<sup>d</sup> CA option to 1981 Federal standards: If select to meet CO 7.0 and NO<sub>x</sub> 0.7 in 1981, must also select these standards in 1982. If select to meet the 1981 Federal standards, must meet CO 7.0 and NO<sub>x</sub> 0.4 in 1982.

#### *Additional Car Requirements*

1981 — No crankcase emissions allowed.

Tampering by service industry, dealers, etc. prohibited. Fuel filler must exclude leaded fuel nozzles (catalyst veh.). Exhaust standards apply to diesel with test modification. Assembly line test requirement-SEA.

Parameter adjustment requirements; idle mixture and choke.

1982 — Diesel particulate std. 0.6 g mi<sup>-1</sup>.

High altitude stds.: Exh. HC 0.57, CO 7.8, NO<sub>x</sub> 1.0 g mi<sup>-1</sup>, evap. 2.6 g per test; altitude waiver stds.: CO 11, NO<sub>x</sub> 1.5.

1984 — All cars meet stds. at all altitudes.

1985 — Diesel particulate std. 0.2 g mi<sup>-1</sup>.

#### *California — In Addition to Federal Car Requirements*

1981 — End-of-line exhaust test.

Fuel filler specs. for vapor recovery-individual veh. delay till 1982 possible depending on extent of body changes.

Higher optional std. for 100,000 mi certification.

Restrictions on allowable maintenance.

“Fixed” idle mixture required.

HFET NO<sub>x</sub> std. 1.33 × FTP std.

Must “meet” CO standard to 6000 ft.

mean emission at 80,450 km to the least squares estimate of the mean emission at 6436 km is called the deterioration factor (df) [15]. The deterioration factors so established are then used to predict the 80,450 km emissions of data vehicles which have been driven for just 6436 km (4000 mi) by multiplying the 6436 km emissions by the deterioration factor. For a vehicle to be certified by the EPA, the extrapolated emission numbers cannot exceed the requirements shown in Table 1.

Emission control requirements have been established in the U.S. for medium and light-duty trucks (Table 2) and for heavy-duty vehicles. Requirements for trucks sold in California are stricter and have different vehicle weight classifications.

**Table 2.** Light/Medium Duty Truck Regulatory Emission Control Requirements<sup>a</sup>

	1981-1983	1984
HC	1.7	0.8
CO	18	10
NO <sub>x</sub>	2.3	2.3

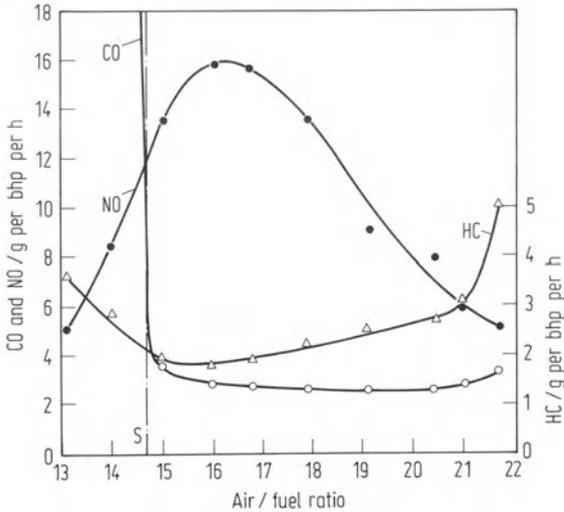
<sup>a</sup> Units are g mi<sup>-1</sup>. Federal definition of light duty trucks is  $\leq 8500$  gross vehicle weight.

The combined effect of new stricter emission control requirements for 1981, changes in the certification regulations over the years, different regulations for vehicles granted waivers, and changes in vehicles in order to simultaneously improve fuel economy and exhaust emissions is the use of many different catalysts by automobile manufacturers on 1981 and 1982 model year vehicles. For example, the total amount of noble metal and the Pt/Pd/Rh ratios differ among catalysts. Some vehicles have single three-way catalytic converters while others have dual-bed catalytic converters for which the first bed operates as a three-way converter, and air is added before the second bed which contains an oxidation catalyst. Catalyst supports are both alumina coated ceramic monoliths and alumina pellets.

### 3. Exhaust Emission Characteristics

The engine-out exhaust emissions of CO, HC, and NO<sub>x</sub> vary as a function of air-fuel ratio as well as several other parameters such as ignition timing and EGR. Here we shall consider only the relationship to air-to-fuel ratio (A/F). A general relationship between engine out CO, HC, and NO<sub>x</sub> emissions and A/F is shown in Figure 1. Engine operation at lean A/F (net oxidizing condition) results in lower HC and CO emissions and more O<sub>2</sub>. These conditions favor subsequent catalytic oxidation reactions. At lean A/F the exhaust contains insufficient reducing agents to react with all the O<sub>2</sub> and all the NO. By operating closer to the stoichiometric A/F more NO

can react but the volume of CO which must be oxidized increases. The stoichiometric A/F occurs at about 14.6. Here, the concentrations of oxidizing gases and reducing gases are matched, and equilibration of the exhaust mixture would yield only CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. The application of three-way catalytic converters has this objective. Three-way catalysts operate in a narrow A/F band between 14 and 15.



**Figure 1.** The effects of air-fuel ratio on hydrocarbon, carbon monoxide, and nitric oxide exhaust emissions. (Reproduced with permission from ref. [11])

The exhaust hydrocarbons are a mixture of olefins, paraffins, and aromatics ranging from C<sub>1</sub> to C<sub>8</sub>. Table 3 lists the important exhaust hydrocarbons [16]. The total and relative concentrations will vary depending upon the A/F and spark timing [16]. Other exhaust constituents include hydrogen which is present at a concentration of about 1/3 that of CO. Water vapor and carbon dioxide concentrations are each about 10% by volume. Sulfur dioxide emissions are 20 ppm for a corresponding sulfur level in the fuel of 0.03 wt%. The use of alternative fuels such as ethanol and methanol leads to an increase in the fraction of exhaust hydrocarbons emitted as aldehydes.

Other exhaust constituents which are significant because they can lead to deterioration of catalyst performance are phosphorus and lead. Phosphorus is present in the fuel (typically 0.02–0.1 mg P l<sup>-1</sup>) but can also be derived from oil consumption. Motor oil typically contains 1.2 g P l<sup>-1</sup>. Lead (as tetraethyl lead) is present at low levels (1 mg Pb l<sup>-1</sup>) in unleaded fuel.

Engine-out emissions of HC, CO, and NO<sub>x</sub> measured during FTP tests have been observed to fall within the following ranges: 1.3 to 2.5 g mi<sup>-1</sup> HC, 10 to 17 g mi<sup>-1</sup> CO, and 0.8 to 2.0 g mi<sup>-1</sup> NO<sub>x</sub> [17]. In order for these engine-out emissions to fall below the 1981 Federal emission control requirements (0.41 HC, 3.4 CO, 1.0 NO<sub>x</sub>), percentage conversions of 70 to 90 percent for HC, 66 to 80 percent for CO, and 0 to 50 percent for NO<sub>x</sub> are required.

**Table 3.** Important Exhaust Hydrocarbons. Summary of Results by Model Year

	1970	1972	1973	1974	1975	1976	1977
No. of Calif. Cars	—	1	—	1	5	—	4
No. of Fed. Cars	1	—	3	8	9	2	—
Mileage	3600	42105	19802	9162	16075	3218	9859
Carbon Percent of Total Hydrocarbon							
Nonreactive Hydrocarbons							
Acetylene	7.4	10.7	7.8	7.7	2.5	3.6	0.3
Methane	6.2	6.3	4.9	4.7	11.3	9.8	28.0
Benzene	6.4	3.8	3.4	4.9	3.7	4.8	1.6
Ethane	1.2	0.9	1.0	1.0	2.6	3.0	4.5
Propane	0.1	0.0	0.1	0.1	0.3	0.3	0.3
Nonreactive Total	21.4	21.7	17.1	18.4	20.4	21.6	34.7
Reactive Hydrocarbons							
Ethylene	10.1	15.5	12.8	12.4	7.4	7.2	7.8
Toluene	11.7	11.4	9.1	7.5	6.5	7.2	7.7
Xylenes	9.7	2.3	4.1	7.7	5.9	7.3	2.0
Propylene	8.0	9.6	6.3	6.1	3.1	3.9	1.5
Trimethylpentanes	2.1	3.0	5.5	4.0	6.4	5.0	15.6
<i>n</i> -Butane	1.6	7.0	2.0	4.7	5.3	3.9	7.2
<i>i</i> -Pentane	4.4	5.2	4.5	3.6	5.4	4.5	5.9
Butenes	6.0	2.3	2.9	4.0	2.5	4.2	0.4
Methylpentanes	2.0	1.2	2.9	2.0	3.0	3.2	1.5
<i>n</i> -Pentane	0.6	2.1	1.4	1.8	2.1	2.1	0.8
Ethylbenzene	1.7	0.6	1.1	1.7	1.4	1.9	0.6
<i>i</i> -Butane	0.8	2.3	0.8	0.6	1.0	0.8	0.3
Other Hydrocarbons	19.8	15.6	29.7	25.6	29.6	27.2	14.0
Reactive Total	78.6	78.3	82.9	81.6	79.6	78.4	65.3
Hydrocarbon Classes							
Total Parafins	23.9	34.5	36.8	33.2	52.9	46.4	74.3
Total Olefins	32.0	31.1	25.7	25.8	16.4	17.0	9.9
Acetylene	7.4	10.7	7.8	7.7	2.5	3.6	0.3
Total Aromatics	36.7	23.7	29.7	33.3	28.2	33.0	15.5

Included in the tailpipe emissions will be gases emitted at the start of the test while the catalyst is still below its operating temperature. HC and CO emissions from the first part of the 1975 FTP test are a significant fraction of the total tailpipe emissions.

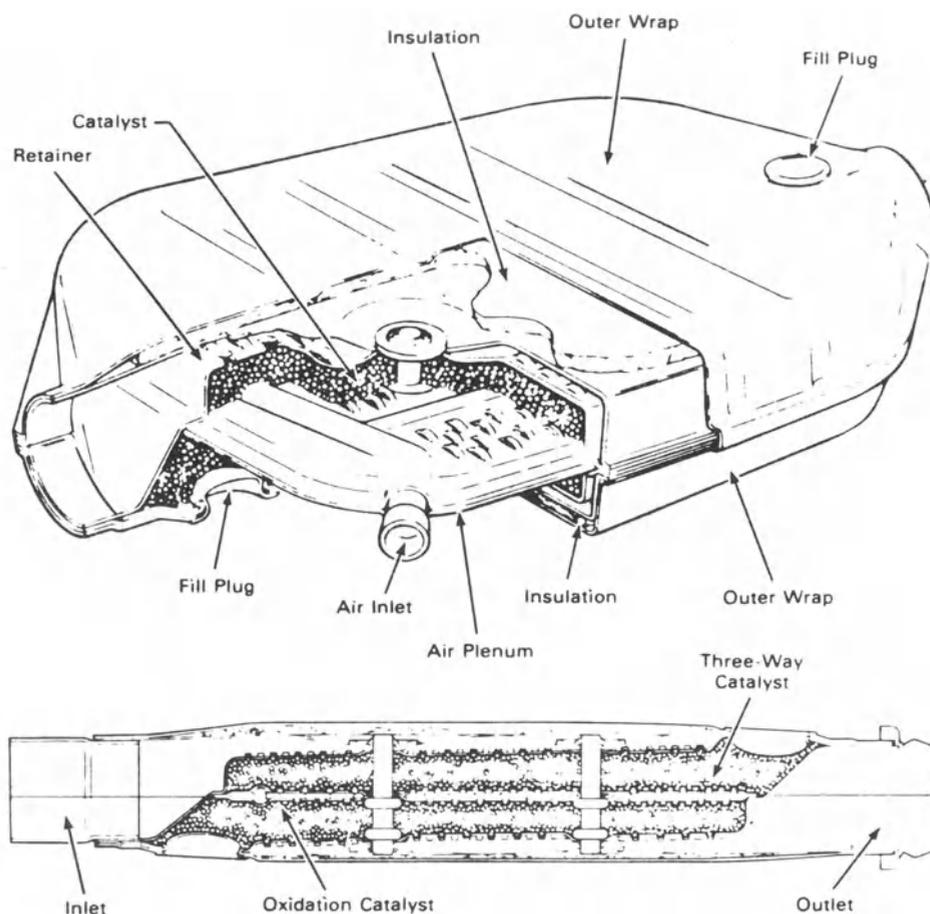
The temperature of the exhaust gases vary depending upon time from start up, engine tuning, engine load, distance from the engine, and heat losses in the exhaust system. Under steady-state conditions exhaust gas temperatures at the inlet to the converter of 673 K to 773 K can be expected.

## 4. 1981 Emission Control Technology

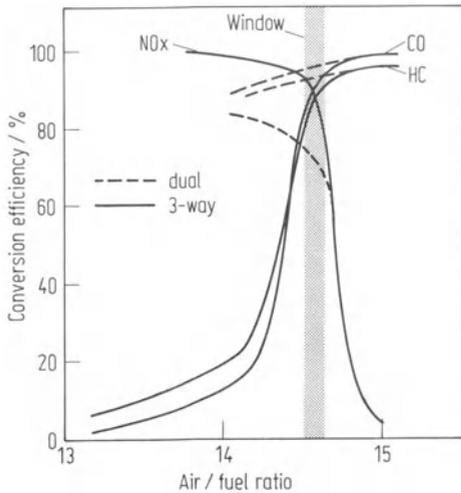
### A. Converters

The catalytic converters used on most 1981 model year vehicles fall into two general categories: three-way converters and dual-bed converters. (Some manufacturers employ dual converters. The distinction between dual-

bed and dual converters is whether the two catalysts are housed in the same container or in separate containers.) Both contain a three-way catalyst, but with the dual-bed converter (and dual converter) the three-way catalyst is followed by an oxidation catalyst to provide increased oxidation capability. Supplemental air is added to the exhaust ahead of the oxidation catalyst. The pellet type dual-bed catalytic converter used by General Motors is shown in Figure 2. Both the three-way catalyst and oxidation catalyst are enclosed in the same converter, separated by the air plenum. Operation of the three-way catalyst requires that the exhaust A/F be controlled close to the stoichiometric composition. A diagram which illustrates the relationship between conversion efficiency and A/F for the two converter types is presented in Figure 3. A closed-loop feed-back control system holds the A/F in a narrow region near stoichiometry.



**Figure 2.** Cross-section of General Motors dual-bed converter. (Reproduced with permission from ref. [18a])



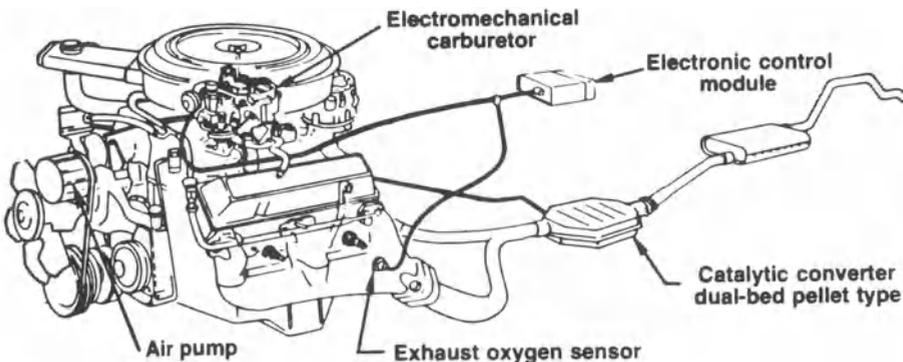
**Figure 3.** Efficiency scan for a dual-bed catalyst and a three-way catalyst. (Reproduced with permission from ref. [18a])

## B. Control System

The basic elements of a closed-loop emission control system are shown in Figure 4. In addition to the catalytic converter (pellet or monolithic type) the system has an exhaust oxygen sensor, electronic control module, carburetor or fuel injector, and air pump [11].

The components of the 1981 General Motors micro-computer engine control system described in a report by Grimm et al. [18, see also 11] will be reviewed here. Reports on other closed-loop A/F control systems with three-way converters are listed in the references [3, 19–22].

The exhaust oxygen sensor indicates whether excess oxygen is present in exhaust. The sensor behaves like a switch in that its output voltage goes through a step change at the stoichiometric point with an A/F change of less than 0.1 A/F unit. The voltage signal from the oxygen sensor passes to the electronic control module and is compared to a preset voltage. The electronic control module then generates a correction control signal which



**Figure 4.** Closed-loop emission control system. (Reproduced with permission from ref. [11])

passes to the carburetor. The control signal increases or decreases at a fixed rate (integral correction) until the oxygen sensor shows that the A/F has crossed the stoichiometric composition; the control signal then reverses following a step change (proportional correction) in the new direction.

The integral and proportional corrections are not fixed but change in value based on input from other signals which follow engine speed and load. The electronic control module therefore receives information on engine coolant temperature, engine speed, throttle position, and manifold pressure. This state-of-the-art system has the potential capability of controlling spark timing, idle speed, exhaust gas recirculation, and transmission converter clutch. It is also able to recognize malfunctioning systems and provides an indication to the driver that a malfunction exists. Appropriate values are then used by the module to permit the vehicle to be operated until the necessary repairs can be made.

The control signal oscillations inherent in the closed-loop system produce oscillations in the exhaust A/F. The amplitude and frequency of the oscillations depend on the transport delay in the engine (manifold and cylinder residence time) and system calibrations. The transport delay decreases as engine speed and/or engine load increases. One cycle per second is a typical oscillation frequency. The closed-loop system is currently the most effective way to maintain the exhaust A/F in the range in which the three-way catalyst simultaneously promotes the reactions of HC, CO, and NO<sub>x</sub>.

Not all 1981 and 1982 model year vehicles have the closed-loop control system; some are operated "open loop". Open loop systems lack the oxygen sensor and feed-back mechanism but retain the three-way or dual catalyst feature. Papers on the development of three-way catalyst systems have been published by several automobile manufacturers. Topics covered include methods for fuel delivery [23], secondary air control [24], catalyst durability [25], and influence of system parameters on catalyst performance [23, 26–30]. The development of closed-loop systems with the research objective of keeping the NO<sub>x</sub> emissions below 0.4 g mi<sup>-1</sup> has been reported by Cederquist *et al.* [31] and Zemke and Gumbleton [18a].

## 5. Catalyst Screening

The automobile manufacturers have developed dynamometer-controlled engine facilities which they use to screen catalysts before certification [30, 32–35]. Aging of catalysts by tests on a dynamometer allows catalyst durability to be measured under precisely controlled conditions and possibly completed in fewer days (by running 24 h days) than for vehicle aging. Dynamometer-controlled engine facilities are used for accelerated aging in which the catalysts are exposed to poisons and high temperatures as well as for short emissions tests. A short description of catalyst screening tests as described in published reports follows.

The AC Spark Plug Division of General Motors has developed a catalytic converter testing facility which consists of a dynamometer-controlled engine,

a gas flow control system, emission analyzers, and a computer interface [32, 33]. Engine operation may be varied according to a simulated driving schedule in order to produce a desired exhaust composition and/or catalyst bed temperature. (The catalyst temperature is of course dependent upon the amount of heat generated by reaction.) Conversely, the exhaust characteristics can be fixed by utilizing a constant schedule, e.g. 80 km h<sup>-1</sup>. Exhaust temperatures and fuel compositions are chosen to be representative of vehicle certification for a given year. For some studies catalytic converters are rotated among a series of engines to ensure that the converters have seen similar conditions [33]. Emission tests are run for these dynamometer aged converters at regular intervals (e.g. 100 h) according to a dynamometer converter performance test [32]. The catalytic conversions of NO<sub>x</sub>, HC, and CO are compared at the start and throughout the 1000 h dynamometer durability test. These durability tests are used to compare catalysts, to test the response of catalysts to fuel compositions (additional Pb, P, or S), and to test the response of catalysts to different aging schedules (exhaust composition, temperature, etc.).

Another catalyst property examined in these dynamometer-controlled engine facilities is the "transient conversion efficiency" of the catalyst, that is, the time required for the catalytic converter initially at ambient temperature to start functioning following a step input of a steady-state exhaust gas [32]. Just CO and HC conversions are monitored in this test because in practice converters are usually warmed up under oxidizing conditions (by addition of air to the exhaust).

With the advent of three-way catalysts durability tests have been developed for which catalyst aging using a dynamometer-controlled engine is followed by a converter performance test in which the A/F is deliberately cycled [30, 34]. For the converter performance tests carried out at the AC Spark Plug Division of General Motors the A/F is cycled  $\pm 0.5$  A/F units at a frequency of 1 Hz about a fixed value. This fixed value is continuously moved very slowly from lean to rich and back over an A/F band of about  $\pm 0.3$  around stoichiometry. Tests of converter performance give information on NO<sub>x</sub>, CO, and HC conversions for fresh and aged catalysts as a function of A/F. Typical conditions are a converter inlet gas temperature of 750 K, exhaust gas flow rate about 33,000 cm<sup>3</sup> s<sup>-1</sup> (293 K, 1 atm), and a corresponding space velocity of 27,900 h<sup>-1</sup> [34].

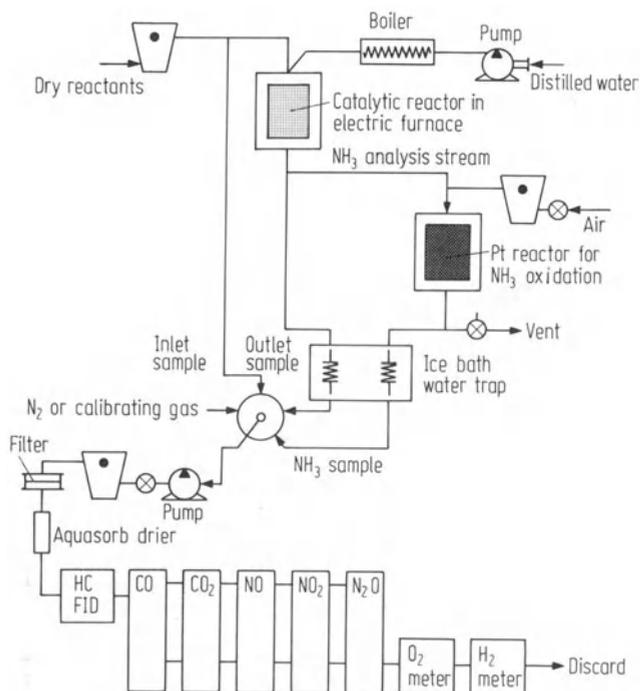
The Ford Motor Company has developed an engine dynamometer test procedure for three-way catalyst screening which like the GM procedure allows for perturbations of the A/F [35]. The Ford aging procedure is *accelerated* compared with the AMA schedule as the test is completed in only 25% of the time of the AMA. Compared with the AMA schedule the number of high speed acceleration (peak temperature) modes is increased fourfold. The fuel lead and phosphorus levels are increased to four times the 1977 certification fuel levels. Just 200 h of dynamometer aging was assumed equivalent to 40,225 km on the standard AMA cycle; a direct comparison of a dynamometer aged catalyst with the same catalyst formulation aged on a vehicle showed the dynamometer aging cycle to be slightly

more severe than vehicle aging. The engine dynamometer catalyst screening procedure involved the measurement of  $\text{NO}_x$ , CO, and HC conversions while the A/F was scanned by applying a DC voltage from a function generator to the electronic control unit. Deliberate oscillations of the A/F around the mean operating point were made by imposing a periodic signal on the DC voltage. Comparison of emission tests with and without A/F oscillations showed that oscillations are necessary to ensure simulation of vehicle operation. For example, for tests of  $\text{NO}_x$  emissions done with A/F oscillations, catalyst rankings agreed with FTP results, whereas screening tests done without perturbations gave different rankings.

## 6. Laboratory Testing

Laboratory testing facilities used for the characterization and preliminary evaluation of three-way catalysts have been described in several reports. Descriptions of several of these reactor systems are given here.

A laboratory reactor used in many studies of automobile emission control catalysts is an integral plug-flow reactor with continuous gas analysis [36–38]. This reactor system allows one to simulate typical exhaust conditions in the laboratory but at the same time provides greater reproducibility and control of conditions than available with dynamometer-controlled engine tests.



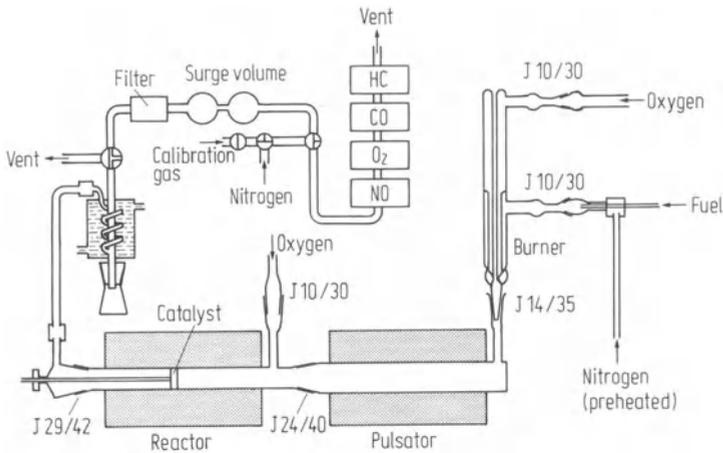
**Figure 5.** Experimental setup for laboratory studies of catalysts. (Reproduced with permission from ref. [36])

An exhaust-like feedstream blended for laboratory experiments typically contains NO (0.05 to 0.2 vol%), CO (0.5 to 2.0 vol%), H<sub>2</sub> (one-third the amount of CO), propylene (0.1 vol% and also propane or methane to simulate less reactive hydrocarbons), CO<sub>2</sub> (10 vol%), H<sub>2</sub>O (10 vol%) and balance N<sub>2</sub>. The integral reactor used by Klimisch and Barnes [36] is shown in Figure 5. The reactor itself is a 3/4 inch I.D. stainless steel pipe. The reactor is situated in an electrical furnace which externally heats the catalyst. A proportional controller regulates the furnace temperature. The gases are preheated as they pass through a 30 cm section of silicon carbide pellets at the inlet to the reactor just ahead of the catalyst. Water vapor is formed by pumping water through a mini pump to a stainless steel coil situated in a furnace close to the reactor inlet. The catalyst temperature is monitored by one or more thermocouples in the catalyst bed. The catalyst bed size is typically 15–30 cm<sup>3</sup>. The gas space velocity can be varied over a wide range but is limited by the size of the reactor at one extreme and the channeling of the gases at the other. Typical values are 10,000 to 50,000 h<sup>-1</sup> (STP). After the gases pass through the reactor the gases are passed through a condenser to remove water vapor. A portion of the exit gases are pumped through the analysis train by a throttled diaphragm pump. The composition of the inlet and outlet gases is determined by comparison with calibration gases.

The continuous gas analyzers used with these laboratory reactors are nondispersive IR for CO, CO<sub>2</sub>, NO, and H<sub>2</sub>O, nondispersive UV for NO<sub>2</sub>, paramagnetic detection for O<sub>2</sub>, and flame ionization detection for hydrocarbons. Either nondispersive IR or chemiluminescence detection is used for NO. Klimisch and Barnes [36] have reported on a convenient method for ammonia determination whereby the gases leaving the reactor are diverted, oxygen added, and passed over a platinum catalyst which quantitatively oxidizes the ammonia back to nitric oxide. The ammonia reading is determined by difference using the NDIR NO analyzer. Breitenbach and Shelef [39] developed a similar technique with a copper oxide catalyst to convert NH<sub>3</sub> to NO. Accurate measurement of H<sub>2</sub> in the effluent is best done by (noncontinuous) gas chromatography.

When sulfur dioxide is included in the laboratory feedstream, certain modifications in the integral reactor system are necessary [40–42]. The reactor tube is changed to Pyrex, and a Goksøyr-Ross coil [43] is added after the catalyst to condense sulfuric acid which is subsequently analyzed by titration of the condensate. A continuous SO<sub>2</sub> analyzer is added to the analysis train. Alternatively SO<sub>2</sub> may be analyzed by sampling through an impinger containing hydrogen peroxide; the sulfate formed is determined by titration [44]. For studies in which the SO<sub>2</sub> is reduced to H<sub>2</sub>S, the H<sub>2</sub>S can be trapped in a buffered zinc acetate solution and analyzed as methylene blue [45, 46].

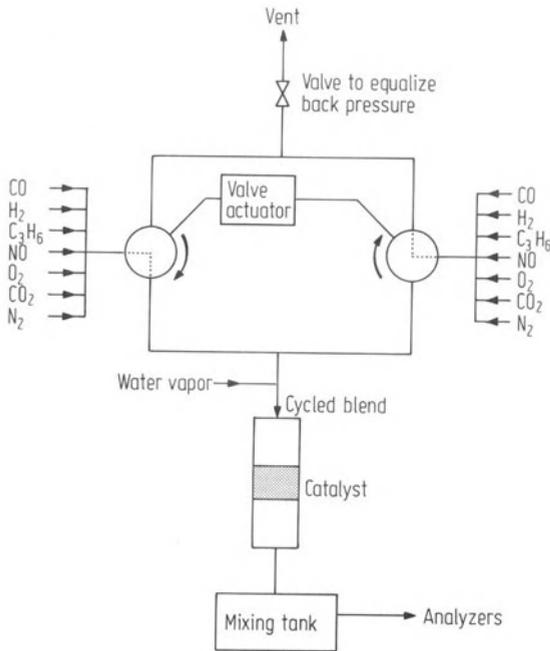
Otto *et al.* [47] developed a “pulse-flame reactor” which utilizes combustion products from a laboratory burner for the feedstream passed over the catalyst. This reactor is suitable for aging catalysts for durability studies because either contaminant-free fuel or fuel doped with lead, phosphorus, and sulfur compounds can be used. A diagram of the pulse-flame apparatus



**Figure 6.** Schematic of pulse flame combustor. (Reproduced with permission from ref. [47])

is shown in Figure 6. The main parts of the system are the feed system, burner, pulsator, catalytic reactor, and analytical instruments for gas analysis. The Pyrex burner is 28 cm in length and 1.7 cm in diameter. Oxygen enters the top of the burner. Preheated nitrogen is mixed with isooctane fuel and enters through another tube so that a combustible mixture forms only near the burner tip. The Vycor pulsator tube which follows is 40 cm in length and 3 cm in diameter. The tube is held at 1023 K. The combustible mixture is heated as it passes through the tube, ignites, burns back to the burner face, and is quenched. This process then repeats itself. The resulting concentration of CO and HC are determined by the oxygen-fuel ratio. The oxygen concentration in the exhaust gases can be adjusted by adding supplemental oxygen just before the reactor. Typical compositions during aging and poisoning are 1.0 vol% CO, 600 ppm HC (as C<sub>6</sub>) 3.5 vol% O<sub>2</sub>, and 0.005 to 0.01 vol% NO. The catalytic reactor is a 55 cm long by 2.4 cm diameter Vycor tube. The catalyst is a small core of a monolith (1.2 cm length by 1.9 cm diameter) precisely cut to fit the reactor. The catalyst temperature is monitored by a thermocouple at its outlet. The space velocity is a nominal 40,000 h<sup>-1</sup> (293 K, 1 atm), though higher during a pulse surge.

Schlatter *et al.* [48] have developed a laboratory reactor system in which the composition of the feedstream can be made to oscillate. The frequency and amplitude of the oscillations can be varied independently. This laboratory reactor is used to investigate the behavior of three-way catalysts in an environment which resembles the exhaust A/F fluctuations in a closed-loop emission control system. A schematic diagram of the system appears in Figure 7. Two gas blending systems, each complete with flow controller and mass flow meters, are used to establish the composition of the individual feedstreams. Two fast-acting solenoid selector valves allow one to cycle between the two feedstreams at a switching frequency which can



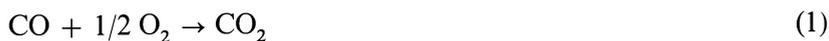
**Figure 7.** Schematic diagram of system for exposing catalyst to an oscillating feedstream composition. The apparatus was used to make the measurements shown in Figures 19, 20, and 22. (Reproduced with permission from ref. [48])

be varied from 0.03 to 10 Hz. The choice of the two gas blends determines the amplitude and average composition of the oscillations. Mixing of the two feedstreams in the small volume between the switching valves and the catalyst attenuates the amplitude from the square wave shape, especially when the switching frequency is fast. Schlatter *et al.* [48] have examined this characteristic of their laboratory reactor in some detail. The continuous gas analyzers see only average conversions independent of cycling conditions due to the addition of a 2 l mixing volume to the system after the catalyst.

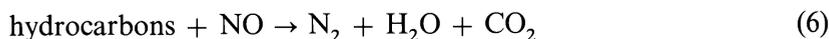
## 7. The Chemical Reactions

The essential requirement for an effective three-way catalyst is high conversions of  $\text{NO}_x$ , CO, and hydrocarbons at and near the stoichiometrically balanced exhaust composition. In general, performance is limited by low conversions of CO and hydrocarbons as the A/F is changed in the reducing (rich) direction and decreased conversion of  $\text{NO}(\text{NO}_x)$  as the A/F is changed in the oxidizing (lean) direction. The narrow range of A/F around the stoichiometric point where conversions are high is commonly referred to as the operating “window”. A wide A/F range or window of high simultaneous  $\text{NO}_x$ , CO, and HC conversions is a desirable catalyst characteristic because it lessens the need for tight A/F control.

The overall catalytic reactions which are important for controlling exhaust emissions are given by the following stoichiometric equations:



as well as



and possibly



The desired products are  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . These reaction products are thermodynamically favored at typical exhaust temperatures, *e.g.* 770 K. The overall conversion is determined not only by the activity of the catalysts to promote reactions 1 to 5 but also by the availability of oxidizing and reducing agents. Oxidizing agents are necessarily in short supply at rich A/F so HC, CO, and  $\text{H}_2$  may be viewed as competing with each other for NO and  $\text{O}_2$ . Reducing agents are in short supply at lean A/F so NO and  $\text{O}_2$  may be viewed as competing for the available  $\text{H}_2$ , CO, and HC. The *selectivity* of the three-way catalyst refers to its tendency to promote CO and HC oxidation (reactions 1 and 2) rather than  $\text{H}_2$  oxidation (reaction 3) at rich A/F and to promote NO reduction (reactions 4, 5, and 6) rather than  $\text{H}_2$  oxidation (reaction 3) and to some extent  $\text{O}_2$  reduction by CO (CO oxidation, reaction 1) at lean A/F. In addition, selectivity refers to the tendency of the three-way catalyst to reduce NO to  $\text{N}_2$  (reactions 4 and 5) rather than to  $\text{NH}_3$  (reaction 7) at rich A/F. Reactions of  $\text{H}_2\text{O}$  with CO (water-gas shift) and hydrocarbons (steam reforming) may contribute to the conversions of CO and HC under net reducing conditions. In exhaust, sufficient reactants are present to completely react NO, CO, and HC over the entire A/F range if we could catalyze particular reactions while suppressing others.

One goal of research and development work on three-way catalyst formulation is to improve catalyst selectivity. As an example, Schlatter and Taylor [49] have demonstrated that three-way catalysts which contain Pd can be less

selective for reducing NO to N<sub>2</sub> than are catalysts which contain only Rh or Pt and Rh after exposure of the catalysts to higher temperatures. The Pd containing catalyst reduced more NO to NH<sub>3</sub> under rich conditions and less NO to N<sub>2</sub> under lean conditions than did the Rh and Pt-Rh catalyst [49]. The results may be explained by the greater tendency of Pd to reduce NO to NH<sub>3</sub> compared with Rh, the consumption of CO by reaction 1 over Pd at the expense of reaction 4, and the sintering of Pt during the high temperature oxidation treatment so that its contribution to reactions 1 and 7 was diminished.

The competition among reactants and the selection of reactants by the catalyst largely determines the effectiveness of the three-way catalyst. Laboratory studies of a single reaction such as  $2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$  tell us whether a particular catalyst can catalyze this reaction but do not tell us whether this reaction is solely responsible for the reduction of NO to N<sub>2</sub> in exhaust. Also no single reaction has been identified which can be used for catalyst evaluations in order that a simple feed may substitute for the exhaust-like feed. Laboratory studies of three-way catalysts are therefore carried out using feeds of varying complexity and at a range of concentrations and temperatures in order to obtain a view of the relative contribution of the catalytic reactions 1 through 13 to the overall conversions. Differences in the detailed chemical mechanisms represented by these overall reactions are to be expected as the catalyst composition is changed. The reader should also note that the conversion of NO, CO, and HC in exhaust will be influenced by the promoting or inhibiting effects of all species in exhaust, not just reactant concentrations. Also two sequential chemical reactions may contribute to the overall conversion. For example, ammonia formed by the reaction of NO with inlet H<sub>2</sub> (or with H<sub>2</sub> produced by the water-gas shift reaction) may decompose in a second reaction to yield N<sub>2</sub>. Such a mechanism has been shown to contribute to NO reduction over alumina supported Pt—Ni catalysts under reducing conditions [50].

A brief discussion of NO reduction chemistry follows. The literature on fundamental studies of CO and HC oxidation will not be reviewed here.

A complete and detailed chemical mechanism by which NO is reduced to N<sub>2</sub> over Rh containing three-way catalysts in exhaust is not known. Several recent studies of the reduction of NO over Rh single crystal surfaces, over polycrystalline Rh wires, and over supported Rh have made an important contribution to our understanding of the mechanism [51–52]. For example, mechanistic studies of the NO—CO reaction over polycrystalline Rh wire [52] and a Rh(331) single crystal [51] have led to the proposed mechanism for NO reduction to N<sub>2</sub> whereby NO dissociation on Rh is followed by N<sub>2</sub> desorption and the reaction of an intermediate surface oxygen specie with CO to form CO<sub>2</sub>. Campbell and White [52] reported that thermal desorption of co-adsorbed NO and CO from polycrystalline Rh produced simultaneous CO<sub>2</sub> and N<sub>2</sub> peaks at 480 K and concluded from this result that the reaction is rate limited by the dissociation of NO. From steady-state kinetic measurements of the NO—CO reaction at constant reactant pressures of  $3.2 \times 10^{-6}$  Pa, Campbell and White [52] observed a