EPA/AA/CTAB/88-10

Technical Report

Methanol Vehicle Catalyst Evaluation: Phase III

by

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November 1988

NOTICE

Technical Reports do not necessarily represent final EPA decisions or positions. They are intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position or regulatory action.

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Office of Air and Radiation
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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OFFICE OF
AIR AND RADIATION

DEC 19 1988

MEMORANDUM

SUBJECT: Exemption From Peer and Administrative Review

FROM: Karl H. Hellman, Chief
Control Technology and Applications Branch

TO: Charles L. Gray, Jr., Director
Emission Control Technology Division

The attached report entitled "Methanol Vehicle Catalyst Evaluation: Phase III," (EPA/AA/CTAB/88-10) describes the evaluation of several noble and base metal catalyst technologies for their use as neat methanol-fueled vehicle catalysts.

Since this report is concerned only with the presentation of data and its analysis and does not involve matters of policy or regulations, your concurrence is requested to waive administrative review according to the policy outlined in your directive of April 22, 1982.

Concurrence: Charles L. Gray, Jr. Date: 12-14-88
Charles L. Gray, Jr., Dir., ECTD

Nonconcurrence: _____ Date: _____
Charles L. Gray, Jr., Dir., ECTD

cc: E. Burger, ECTD

I. Summary

The methanol catalyst testing reported on here was conducted as a follow-up to an earlier EPA catalyst evaluation program.[1,2,3,4] The purpose of the testing described here in Part 1, Section V was to evaluate noble metal catalysts suggested by researchers to be particularly effective for methanol-vehicle applications.[5,6] The purpose of the testing described in Part 2, Section V was to evaluate selected base metals and other specific catalyst technologies for use as methanol-vehicle catalysts.

Both of the configurations tested in Part 1, Ag:Pd(50) and Pt(50), were effective when tested as three-way catalysts over the Federal test procedure (FTP). The formaldehyde emission level was only 5.9 milligrams per mile over the FTP in the three-way mode with the Pt(50) catalyst. The simulated oxidation catalyst mode was not preferred to the three-way mode because of considerably higher NOx and formaldehyde emissions. Both catalysts had good HC, CO, and formaldehyde conversion efficiencies over the highway fuel economy test (HFET) cycle.

The base metal/palladium and platinum/palladium/unique washcoat configurations discussed in Part 2 had HC efficiencies greater than 90 percent over the FTP. CO emissions from the test vehicle were low, only 0.73 grams per mile over the FTP, when the base metal/palladium catalyst was used. NOx emissions with these catalysts were relatively unchanged from baseline levels. Both base metal-containing catalysts also had formaldehyde conversion efficiencies greater than 90 percent over the FTP.

II. Introduction

Section 211 of the Clean Air Act [7] requires the U.S. Environmental Protection Agency (EPA) to play a key role in the introduction of new motor vehicle fuels. EPA studies [8] have suggested that methanol stands out from other alternative transportation fuels from an environmental perspective. The use of alcohol fuels can also play a significant role in the reduction of the foreign trade deficit and aid the security interests of the United States by reducing U.S. dependence on imported petroleum.[9]

The use of methanol fuel rather than gasoline may be expected to benefit the performance of a catalytic converter in two ways. First, pure methanol contains low levels of substances such as sulfur and lead which act as catalyst poisons. Second, reduced exhaust gas temperatures at the catalyst inlet should reduce thermal degradation over an extended period of vehicle operation.

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The emission control system was modified by EPA to include an air injection pump which can inject air into the exhaust at a location approximately 1 foot downstream from the oxygen sensor. A manually adjustable valve was installed in the line between the diverter valve and the exhaust inlet. The valve permits the oxygen concentration over the catalyst to be varied while operating the engine in the closed-loop mode.

A detailed description of the vehicle and special methanol modifications is provided in Appendix A.

The test vehicle referred to in Part 2, Section V was a 1986 Toyota Carina, a vehicle sold in Japan but currently not exported to the United States. The powerplant is a 1587 cc displacement, 4-cylinder, single-overhead camshaft engine. The engine has been modified for operation on methanol in a lean burn mode, incorporating the lean mixture sensor, swirl control valve and timed sequential fuel injection found on the Toyota lean combustion system (T-LCS). Modifications to the fuel system included the substitution of parts resistant to methanol corrosion for stock parts.

A detailed description of the vehicle and special methanol modifications is provided in Appendix B.

IV. Test Facilities and Analytical Methods

Emissions testing at EPA was conducted on a Clayton Model ECE-50 double-roll chassis dynamometer, using a direct-drive variable inertia flywheel unit and road load power control unit. The Philco Ford CVS used has a nominal capacity of 350 cfm.

Exhaust HC emissions were measured by flame ionization detection (FID) using a Beckman Model 400. This FID was calibrated with propane; no attempt was made to adjust for FID response factor to methanol. No corrections were made for the difference in hydrocarbon composition due to the use of methanol rather than unleaded gasoline for fuel. NOx emissions were measured by chemiluminescent technique utilizing a Beckman Model 8501-5CA.

Exhaust formaldehyde is measured using a dinitrophenylhydrazine (DNPH) technique.[12,13] Exhaust carbonyls including formaldehyde are reacted with DNPH solution forming hydrazone derivatives. These derivatives are separated from the DNPH solution by means of high performance liquid chromatography (HPLC). Quantization is accomplished by spectrophotometric analysis of the LC effluent stream.

HC test results in the text are presented without accounting for FID response to methanol or the difference in HC composition because of the use of methanol fuel. The emission values presented in this report were also calculated using proposed methanol-fueled vehicle test procedures.

The Emission Control Technology Division (ECTD) of the Office of Mobile Sources, EPA, assesses technology that could be used to reduce mobile source emissions. One part of this assessment has been a program to evaluate various exhaust catalysts at low mileage on neat methanol-fueled (M100) vehicles. Test results from this program have been published in a variety of EPA and other professional literature sources.[1,2,3,4]

The testing discussed in this report has been divided into two separate sections. The first section discusses the evaluation of two noble metal catalysts: 1) Platinum, at 50 grams per cubic foot of substrate volume, and 2) a silver/palladium mixture, also at 50 grams per cubic foot of substrate volume. These catalysts were supplied to EPA by Engelhard Industries; specifications are provided in Section V of this report.

Two different catalyst operating modes were chosen for Part 1. The catalysts were first tested as three-way converters, to oxidize unburned fuel, aldehydes, and CO as well as to reduce NOx emissions. An air pump which supplied air to the exhaust ahead of the catalyst but downstream of the exhaust oxygen sensor was then used to evaluate the catalysts in a simulated oxidation mode. The driving cycles tested were the Federal test procedure (FTP) [10] and the highway fuel economy test (HFET) [11] cycles.

Part 2 of Section V in this report discusses the evaluation of three catalysts obtained from Automotive Catalyst Company, a subsidiary of Allied-Signal. These catalysts utilized in turn:

1. A base-metal only technology;

2. A mixture of base metal and palladium; and

3. A platinum-palladium mixture utilizing a unique washcoat.

The details of the catalyst formulation and application are proprietary to Allied-Signal.

III. Vehicle Descriptions

The vehicle used for the noble metal catalyst screening described in Part 1, Section V was a 1981 Volkswagen Rabbit 4-door sedan, equipped with automatic transmission, air conditioning, and radial tires. The 1.6-liter engine is rated at maximum power output of 88 horsepower at 5,600 rpm. The vehicle was tested at 2,500 lbs inertia weight and 7.3 actual dynamometer horsepower.

V. Part 1: Noble Metal Catalyst Screening

A. Program Design

The evaluation of a catalyst during this phase was a three-step process. First, the test vehicle was emission-tested on a chassis dynamometer without the catalytic converter present in the exhaust stream and with the air pump rendered inoperable. The driving cycles tested were the FTP and HFET.

Following these baseline tests, the catalyst to be evaluated was attached under the vehicle in the exhaust stream. The catalyst was evaluated in an underfloor location. The second step of the process was to repeat the series of tests described above with the air pump still disabled. The catalyst was evaluated in the "three-way" mode in this test.

In the third step, the air pump was enabled and air was added at a predetermined rate to the exhaust directly in front of the catalyst but downstream of the oxygen sensor. This action simulated the operation of the catalyst as an oxidation catalyst. The amount of air supplied by the air pump during testing was the amount of necessary makeup air to obtain 3 percent oxygen in the vehicle exhaust (at the catalyst inlet) at 30 MPH steady-state conditions as measured with a Sun oxygen analyzer. The car was then tested over the FTP and HFET cycles in this configuration. Following this oxidation catalyst mode testing the converter was removed from the exhaust stream, the air pump was disabled, and the car was again baseline tested.

B. Catalysts Tested: Part 1

The catalysts reported on here used ceramic monolithic substrates which contained 400 square cells per square inch. The substrates were cylindrically shaped, 4.0 inches in diameter and 6.0 inches in length.

The catalyst descriptions indicate the ratio of the constituents by weight, and the number in parentheses at the end of the description gives the catalyst loading in grams per cubic foot. Constituents are identified by their chemical abbreviations.

Other details of catalyst formulation, application and structure are considered proprietary to Engelhard Industries.

C. FTP Test Discussion

FTP test results are presented and analyzed here in two formats. Table 1 details emission levels from the evaluated converters obtained over two catalyst operating modes, three-way and oxidation catalyst, respectively. Baseline (no catalyst) results with the air pump disabled are also presented for each pollutant category. The discussion below includes a determination of the most effective operating mode for these catalysts.

Table 1

Emissions Test Results

VW Rabbit Vehicle, M100 Fuel, FTP Cycle

Configuration	Number of Tests	HC (g/mi)	HC* (g/mi)	CO (g/mi)	NOx (g/mi)	CH3OH* (g/mi)	OMHCE* (g/mi)	Alde. (mg/mi)
Baseline	3	1.02	0.12	6.45	1.67	2.78	1.47	302.0
Ag:Pd(50) 3-way	3	0.18	0.02	0.68	0.96	0.48	0.24	17.6
Ag:Pd(50) Oxid.	3	0.25	0.03	0.48	1.82	0.68	0.38	115.0
Pt(50) 3-way	3	0.18	0.02	0.45	0.95	0.49	0.24	5.9
Pt(50) Oxid.	2	0.16	0.02	0.34	1.84	0.42	0.21	8.9

* Calculated values per proposed rulemaking.

HC and CO emissions were 0.18 and 0.68 grams per mile respectively over the FTP with the Ag:Pd (50) catalyst in the three-way mode. HC increased to 0.25 grams per mile when the catalyst was tested in the oxidation mode. The addition of air assisted the oxidation of CO, however; CO dropped to 0.48 grams per mile over the FTP with the air pump on. HC emissions from the Pt(50) converter were a similar 0.18 and 0.16 grams per mile respectively over the three-way and oxidation catalyst modes. The addition of air appeared to assist the conversion of CO with the Pt(50) converter, as was the case with the Ag:Pd(50) catalyst; CO dropped to 0.34 grams per mile with the air pump on, versus 0.45 grams per mile in the three-way mode.

NOx emission levels were similar for both catalysts in the three-way mode over the FTP, approximately 0.95 grams per mile. The addition of air caused NOx emissions from both catalysts to rise to similar levels of approximately 1.8 grams per mile. The Pt(50) catalyst reduced emissions of formaldehyde to 5.9 milligrams per mile over the FTP in the three-way mode; formaldehyde emissions were 17.6 milligrams per mile with the Ag:Pd(50) catalyst in the same mode. The use of additional air caused formaldehyde levels to increase substantially with both catalysts; formaldehyde levels of 115 milligrams per mile over the FTP were noted with the Ag:Pd(50) catalyst in the oxidation mode. The increase in formaldehyde emissions from the Pt(50) catalyst, from 5.9 (three-way) to 8.9 milligrams per mile when tested in the oxidation mode was substantial; however, the efficiency of the Pt(50) catalyst exceeded 97 percent in the oxidation mode.

The three-way catalyst mode appears to be the preferred operating mode when all pollutants are considered to be of equal concern. HC levels were determined to be approximately 0.16 to 0.18 grams per mile for each configuration with the exception of 0.25 grams per mile from the Ag:Pd(50) catalyst in the oxidation mode. The oxidation mode was preferred for CO conversion, increasing conversion efficiency by 25 to 30 percent for the catalysts evaluated. The three-way mode was clearly preferred for NOx and formaldehyde, however. Overall, despite the suggestion that CO conversion is assisted by the addition of excess air, the three-way mode, because of its simplicity and superiority in reducing formaldehyde and NOx emissions and the lack of convincing evidence that HC efficiency was significantly improved by the addition of excess air, was preferred.

Figures 1 and 2 compare the results from the evaluated catalysts over the three-way mode to heavily loaded noble metal catalyst test results obtained [4] with this vehicle. The catalysts used for this comparison were 5Pt:Rh(80) and Ag:Rh(300) coated ceramic monoliths of the same physical size and exhaust stream location as the catalysts evaluated here.

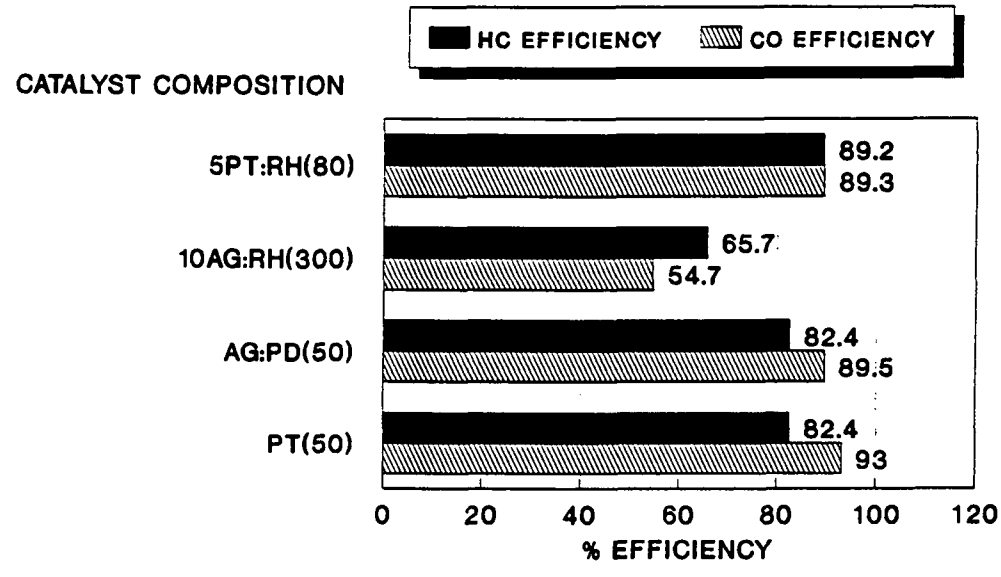

FIGURE 1

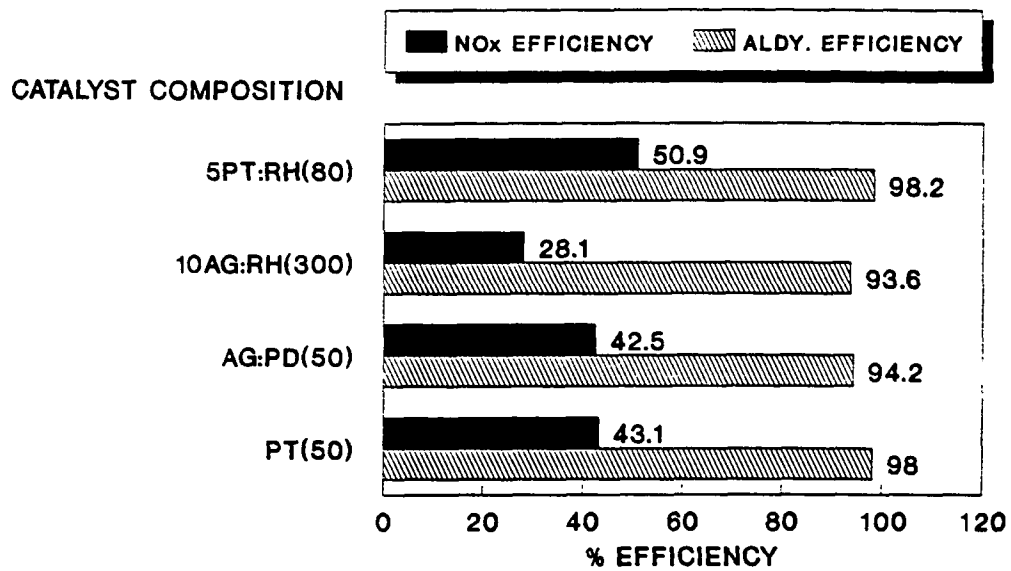

FIGURE 2

Both of the evaluated catalysts had HC efficiencies of 82.4 percent, slightly lower than the 89.2 percent efficiency obtained with the more heavily loaded 5Pt:Rh(80) catalyst. The use of palladium rather than rhodium, at least in the proportions tested here, appeared to be preferred when used with silver for HC conversion. The evaluated catalysts also had CO conversion efficiencies slightly higher than that previously experienced with the 5Pt:Rh(80) catalyst. The increase in efficiencies was marginal, however; Ag:Pd(50) had a 89.6 percent efficiency compared with 89.3 percent for 5 Pt:Rh(80).

NOx efficiencies for the evaluated catalysts were similar, 42.5 and 43.1 percent respectively for the Ag:Pd(50) and Pt(50) catalysts. These were slightly lower than the 50.9 percent efficiency from the 5Pt:Rh(80) catalyst, yet a substantial improvement from the 28.1 percent from the 10Ag:Rh(300) catalyst. Both evaluated catalysts had NOx levels which approximated the current 1 gram per mile light-duty vehicle NOx standard.

Formaldehyde efficiencies for all catalysts referred to here were uniformly high; however, the silver-containing catalysts performed less efficiently than the platinum-containing catalysts. Silver-containing catalysts had formaldehyde conversion efficiencies of 94 percent; these efficiencies were consistent despite the widely varying formulations between the catalysts because of the addition of other noble metals. The platinum-containing catalysts had a consistent 98 percent formaldehyde efficiency; platinum appears to be a very good catalyst for conversion of formaldehyde in vehicle exhaust.

The three-way operating mode was preferable to the oxidation mode for the catalysts evaluated, when the pollutants measured are considered to be equally undesirable. Similar catalyst efficiencies were noted for HC and NOx conversion for both the Ag:Pd(50) and Pt(50) catalysts. The Pt(50) catalyst was slightly more efficient than Ag:Pd(50) at controlling formaldehyde and CO emissions.

D. HFET Test Discussion

HFET results are presented in Table 2. The same format that was used in Table 1, FTP Results, is used here.

Table 2

Emissions Test Results

VW Rabbit Vehicle, M100 Fuel, HFET Cycle

Configuration	Number of Tests	HC (g/mi)	HC* (g/mi)	CO (g/mi)	NOx (g/mi)	CH3OH* (g/mi)	OMHCE* (g/mi)	Alde. (mg/mi)
Baseline	1	0.56	.07	5.30	2.81	1.53	0.79	128.0
Ag:Pd(50) 3-way	3	0.01	--	0.01	1.53	0.03	0.02	3.6
Ag:Pd(50) Oxid.	3	0.01	--	--	2.78	0.04	0.02	9.4
Pt(50) 3-way	3	0.01	--	--	1.43	0.02	0.01	1.9
Pt(50) Oxid.	2	0.01	--	--	2.91	0.03	0.01	1.6

* Calculated values per proposed rulemaking.

-- No detectable levels.

All of the catalysts tested reduced HC emissions to very low levels over both operating modes. This was not unexpected due to the high speed driving characteristics of the cycle which caused catalysts to light-off very early. The oxidation reactions which produced lower aldehyde and CO emissions were similarly affected. The Ag:Pd(50) catalyst had a substantially lower formaldehyde conversion efficiency in the oxidation mode than in the three-way mode. NOx levels from both evaluated catalysts approximated baseline levels when tested in the oxidation mode. NOx efficiencies approximated 47 percent from both catalysts when tested in the three-way mode.

VI. Part 2: Base Metal/Alternative Technology Catalyst Screening

A. Program Design

The evaluation of the catalysts during this phase was a three-step process. First, the car was emission tested on a chassis dynamometer with an uncatalyzed substrate present in the stock catalytic converter can on the vehicle. This testing was defined as baseline testing for this report. The original equipment (OEM) converter for the M100-fueled Toyota Carina vehicle used in this testing is close-coupled to the exhaust manifold, rather than located underfloor. The driving cycles were the FTP and HFET cycles.

Following these baseline tests, the uncatalyzed substrate was replaced with the OEM Pt:Rh catalyzed substrate and the vehicle was tested over FTP and HFET cycles. This testing is referred to later in the discussion as OEM manifold converter testing.

The candidate catalysts were then mounted in the exhaust stream in an underfloor location and separately evaluated over FTP and HFET cycles. The uncatalyzed substrate was placed in the exhaust at the exhaust manifold location during the separate underfloor catalyst evaluations.

The catalysts were not evaluated here in the oxidation mode for two reasons. First, we believed that the three-way mode was preferable for the reasons given in Section V, Part 1 of this report. Second, the test vehicle operates lean of stoichiometric by design.[14]

B. Catalysts Tested: Part 2

The catalysts reported on here used ceramic monolithic substrates of the same dimensions as the substrates described in Part 1. The three catalysts reported on in this section made use of:

1. Base-metal-only technology;

2. A mixture of base metal and palladium; and

3. A platinum-palladium mixture utilizing a unique washcoat.

The third technology is referred to as Pt/Pd/coat in Figures 3 and 4.

The details of the catalyst formulations are proprietary to Allied-Signal.

C. FTP Test Discussion

Results of testing over the FTP cycle are presented in Table 3 and Figures 3 and 4.

Table 3

Emissions Test Results

Toyota Carina, M100 Fuel, FTP Cycle

Configuration	Number of Tests	HC (g/mi)	HC* (g/mi)	CO (g/mi)	NOx (g/mi)	CH3OH* (g/mi)	OMHCE* (g/mi)	Alde. (mg/mi)
Baseline	4	1.67	0.200	4.26	1.11	4.55	2.36	419.
OEM manifold converter	3	0.07	0.008	1.84	0.73	0.19	0.09	11.
Base metal converter	3	0.38	0.044	1.08	1.24	1.02	0.50	34.
Base metal and Pd	3	0.14	0.017	0.73	1.16	0.39	0.20	30.
Pt/Pd, unique washcoat	2	0.13	0.016	1.62	1.01	0.36	0.19	56.

* Calculated values per proposed rulemaking.

HC levels from the OEM manifold converter were 0.07 grams per mile for an efficiency of almost 96 percent. The noble metal-containing catalysts had similar efficiencies exceeding 90 percent, yet the weight per mile of HC allowed by these catalysts was almost twice the level from the OEM converter. The efficiency of the base metal converter was considerably lower at 77 percent.

CO levels from the OEM converter exceeded those from each underfloor catalyst tested. The base metal and palladium configuration had a CO efficiency at 82.9 percent, considerably higher than the OEM converter. The base metal converter reduced CO emissions by almost 75 percent, better than the 62 percent decrease in CO with the platinum/palladium catalyst.

NOx levels in some cases exceeded baseline emissions. The OEM converter had the lowest NOx levels, 0.73 grams per mile over the FTP for an efficiency of 34 percent. Each of the evaluated converters had NOx emissions in excess of the current 1 gram per mile light-duty vehicle standard, though the platinum/palladium catalyst came close to meeting the standard at 1.01 grams per mile NOx. The base metal containing catalysts each had NOx levels exceeding baseline levels; Figure 4 does not reflect this negative efficiency, however.

Aldehyde efficiencies from each of the evaluated catalysts were uniformly high, exceeding 85 percent. The OEM manifold close-coupled converter had the highest efficiency though, 97.4 percent. This high efficiency was probably the result of the catalysts' location close to the engine, allowing for a very fast warmup and hence, quick light off. Both base metal-containing catalysts tested here had formaldehyde efficiencies greater than 90 percent; even at these high conversion efficiencies, however, these catalysts allowed almost three times the mass of formaldehyde emitted over the FTP when compared to the manifold close-coupled converter.

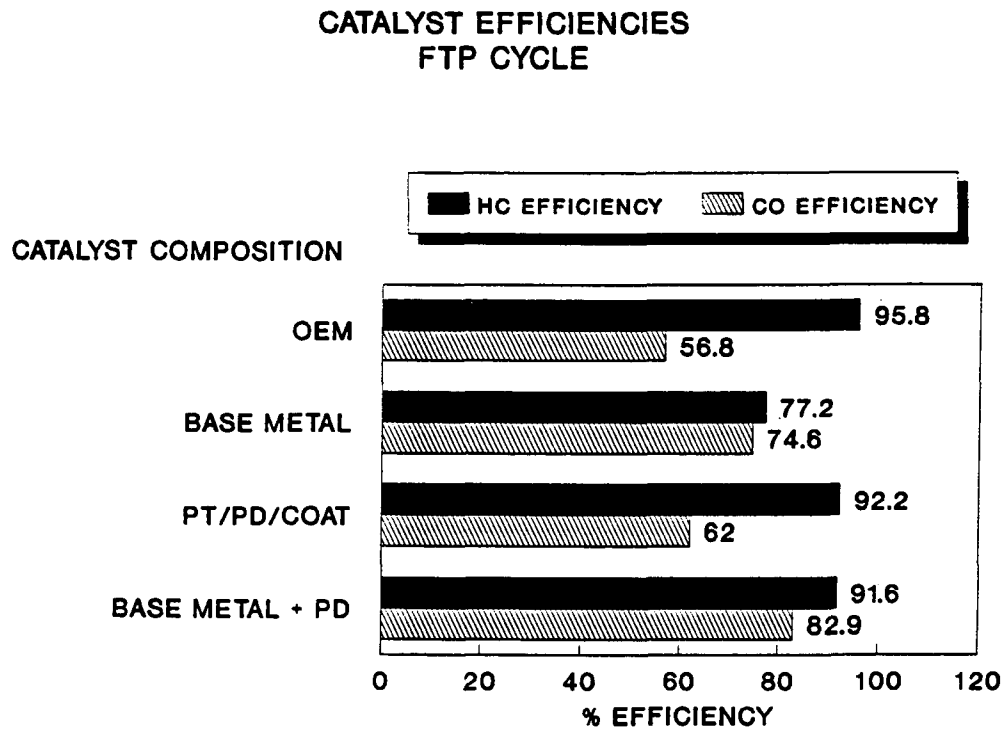

FIGURE 3

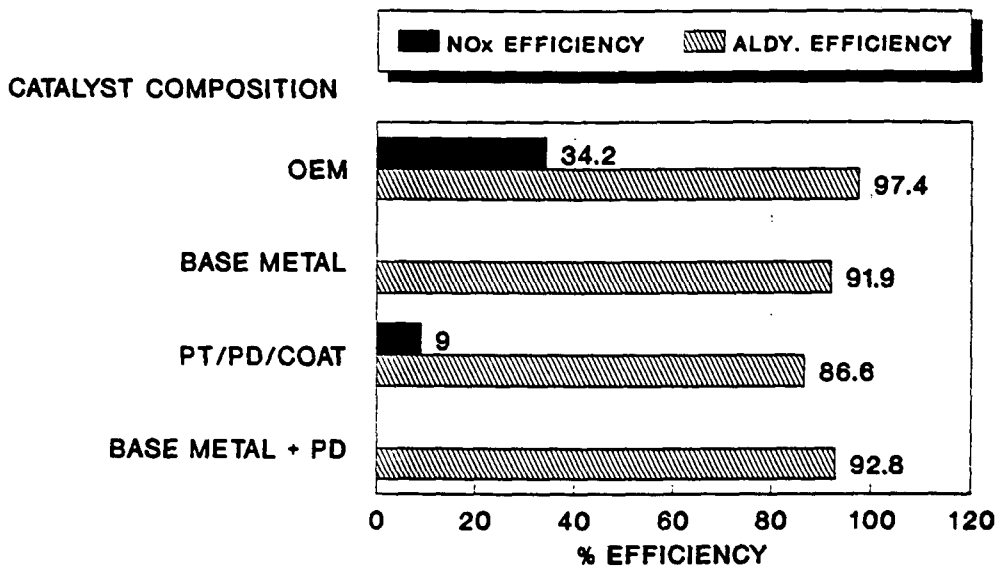

FIGURE 4

D. HFET Test Discussion

HFET test results are given in Table 4.

Table 4

Emissions Test Results

Toyota Carina, M100 Fuel, HFET Cycle

Configuration	Number of Tests	HC (g/mi)	HC* (g/mi)	CO (g/mi)	NOx (g/mi)	CH3OH* (g/mi)	OMHCE* (g/mi)	Alde. (mg/mi)
Baseline	4	0.94	0.11	1.65	0.83	2.57	1.29	134.
OEM manifold converter	1	0.005	0.001	0.13	0.83	0.01	0.01	8.
Base metal converter	3	0.007	0.001	0.01	1.05	0.02	0.01	3.
Base metal and Pd	3	0.003	--	--	1.05	0.01	0.01	3.
Pt/Pd, unique washcoat	2	0.003	0.001	0.09	0.94	0.01	0.01	6.

* Calculated values per proposed rulemaking.
-- No detectable levels.

HC, CO and formaldehyde emission levels were uniformly low when compared to baseline levels. The base metal-containing catalyst had higher CO and formaldehyde efficiencies than the manifold close-coupled and platinum/palladium underfloor catalysts. The base metal-containing catalysts had NOx levels of 1.05 grams per mile, however, which exceeded baseline levels.

VII. Test Highlights

A. Part 1

1. Both Ag:Pd(50) and Pt(50) configurations in the three-way mode had similar HC and NOx efficiencies from baseline levels over the FTP of 82 and 43 percent, respectively. A more heavily loaded platinum/rhodium converter had HC and NOx efficiencies from baseline of 89 and 51 percent, respectively, in the same mode.

2. Formaldehyde levels over the FTP were lowest (5.9 mg/mi) from the Pt(50) catalyst in the three-way configuration. Formaldehyde and NOx levels generally increased from all catalysts when the oxidation mode was used.

3. CO levels over the FTP were generally lower in oxidation mode testing. In the three-way mode, the CO emissions from the Ag:Pd(50) and Pt(50) catalysts of 0.68 and 0.45 grams per mile approximated levels from the more heavily loaded 5Pt:Rh(80) converter.

4. The three-way catalyst mode is the preferred operating configuration when all measured pollutants are considered to be of equal concern.

5. HC, CO, and formaldehyde efficiencies over the HFET cycle were generally very high from both catalysts in the three-way mode. NOx efficiencies approximated 47 percent from both catalyts in the three-way mode; NOx emissions rose to baseline levels from both catalysts when tested in the oxidation mode, however.

B. Part 2

1. The lowest HC emissions over the FTP, approximately 0.13 grams per mile, were obtained from the two noble metal-containing catalysts. The OEM converter had an HC emission level of 0.07 grams per mile; the difference may be due to quicker light-off of the OEM converter, which is located closer to the engine.

2. All three evaluated catalysts had higher CO efficiencies over the FTP than the manifold closed-coupled converter.

3. All three evaluated catalysts had lower NOx efficiencies than the manifold close-coupled converter. NOx levels with each evaluated catalyst slightly exceeded the current 1 gram per mile light-duty vehicle standard for NOx.

4. The base metal-containing catalysts had formaldehyde efficiencies exceeding 90 percent over the FTP. The levels of formaldehyde emissions were approximately 30-34 grams per mile over the FTP for these two catalysts.

5. HC, CO, and formaldehyde levels from each evaluated catalyst were low over the HFET cycle. NOx levels from each catalyst exceeded baseline amounts over the HFET, however.

VIII. Acknowledgments

The catalysts described in Section V, Part 1 of this report were provided by Engelhard Industries. The methanol-fueled vehicle used for this testing was supplied to EPA by Volkswagen AG. The catalysts described in Section V, Part 2 were provided by Automotive Catalyst Company, a subsidiary of Allied-Signal. These catalysts were evaluated on a methanol-fueled vehicle supplied by the Toyota Motor Corporation.

The author appreciates the efforts of Ernestine Bulifant, Robert Moss, and Stephen Halfyard of the Test and Evaluation Branch, Emission Control Technology Division, who conducted the driving cycle tests and prepared the formaldehyde samples for analysis.

In addition, the author appreciates the efforts of Jennifer Criss and Marilyn Alff of the Control Technology and Applications Branch, ECTD, whose attention to detail during the typing of the text and the tables was greatly appreciated.

IX. References

1. "Low Mileage Catalyst Evaluation With a Methanol-Fueled Rabbit - Interim Report," Wagner, R. and L. Landman, EPA-AA-CTAB-83/05, May 1983.

2. "Low Mileage Catalyst Evaluation With a Methanol-Fueled Rabbit - Second Interim Report," Wagner, R. and L. Landman, EPA-AA-CTAB-84/03, June 1984.

3. "Evaluation of Catalyst for Methanol-Fueled Vehicles Using a Volkswagen Rabbit Test Vehicle," presented at the Joint Conference On the Introduction and Development of Methanol As An Alternate Fuel, Columbus, OH, June 26-27, 1986, ASME.

4. "Catalysts for Methanol Vehicles", Piotrowski, G. K. and J. D. Murrell, SAE Paper 872052, November, 1987.

5. "Kinetics and Reaction Pathways of Methanol Oxidation on Platinum," McCabe, R. W. and D. F. McCready, Journal of Physical Chemistry, 1986, Vol. 90, pp. 1428-1435.

6. "Exhaust-Catalyst Development For Methanol-Fueled Vehicles: A Comparative Study of Methanol Oxidation Over Alumina-Supported Catalysts Containing Group 9, 10, and 11 Metals," McCabe, R. W. and P.J. Mitchell, Applied Catalysis, Vol. 27, 1986, pp. 83-98.

7. The Clean Air Act As Amended Through July 1981, Section 211(c)(1).

8. Speech by Charles L. Gray, Jr., EPA, OMS, OAR, to 1983 Midyear Refining Meeting of the API, May 11, 1983.

9. Policy Statement to Vice President of the U.S.A., George Bush, March 6, 1987.

10. 1975 Federal Test Procedure, Code of Federal Regulations, Title 40, Part 86, Appendix 1(a), Urban Dynamometer Driving Schedule.

11. Highway Fuel Economy Driving Schedule, Federal Register, Vol. 41, No. 100, May 21, 1976, Appendix 1.

12. Formaldehyde Measurement In Vehicle Exhaust At MVEL, Memorandum, Gilkey, R. L., OAR, OMS, EOD, Ann Arbor, MI, 1981.

13. "Formaldehyde Sampling From Automobile Exhaust: A Hardware Approach," Pigeon, W., EPA-AA-TEB-88/01, July, 1988.

14. "Development of Methanol Lean Burn System," Katoh, K., Y. Imamura and T. Inoue, SAE Paper 860247, February, 1986.

APPENDIX A (cont'd)

Methanol-Powered Volkswagen Test Vehicle
Specifications and Changes To Accommodate Methanol Fuel

Vehicle Item	Specification/Change
Idle Setting	Specific to methanol calibration.
PCV:	PCV valve with calibrated plunger--no orifice.
Ignition:	
Distributor	Slightly reduced maximum centrifugal advance and slightly modified vacuum advance/retard characteristics.
Spark Plugs	Bosch W260T2
Transmission:	
General	1981 production automatic 3-speed.
Torque Converter Ratio	2.44
Stall Speed	2000-2200 RPM
Gear Ratios:	
1	2.55
2	1.45
3	1.00
Axle	3.57
Fuel Tank:	
Material	Steel
Coating	Phosphated steel
Seams and Fittings	Brazed
Cap	European neck and locking cap
Fuel	Neat methanol (M100)

APPENDIX A

Methanol-Powered Volkswagen Test Vehicle
Specifications and Changes To Accommodate Methanol Fuel

Vehicle Item	Specification/Change
Engine:	
Displacement	1.6 liter
Bore	7.95 cm
Stroke	8.00 cm
Compression Ratio	12.5:1
Valvetrain	Overhead camshaft
Basic Engine	GTI basic engine - European high performance engine to withstand higher loads - U.S. cylinder head
Fuel System:	
General	Bosch CIS fuel injection with Lambda feedback control, calibrated for methanol operation
Pump Life	1 year due to corrosiveness of methanol. Improved insulation on wiring exposed to fuel
Accumulator-Maximum Holding Pressure	3.0 Bar
Fuel Filter	One-way check valve deleted because of fuel incompatibility
Fuel Distributor	5.0-5.3 bar system pressure, calibration optimized for methanol, material changes for fuel compatibility
Air Sensor	Modified air flow characteristics.
Fuel Injectors	Material changes for fuel compatibility, plastic screen replaced by metal screen
Cold Start Injectors	2 injectors, valves pulse for 8 seconds beyond start mode below zero degrees centrigrade
Fuel Injection Wiring	Modified for cold start pulse function and to accommodate relays and thermo switch

APPENDIX B (cont'd)

Description of Toyota LCS-M Test Vehicle

Ignition Timing	With check connector shorted, ignition timing should be set to 10°BTDC at idle. With check connector unshorted, ignition timing advance should be set to 15°BTDC at idle. Idle speed is approximately 550-700 rpm
Engine Oil	10W-30(SF). Toyota recommends oil change interval of 3,000 miles
Fuel Injectors	Fuel injectors (main and cold start) capable of high fuel flow rates. The fuel injector bodies have been nickel-plated, and the adjusting pipes are stainless steel.
Fuel Pump	In-tank electric fuel pump with brushless motor to prevent corrosion. The body is nickel plated and its capacity to deliver fuel (flow rate) has been increased.
Fuel Lines and Filter	The tube running from the fuel tank to the fuel filter has been nickel plated. The fuel filter, located in the engine compartment, has also been nickel plated. The fuel delivery rail has been plated with nickel-phosphorus.
Catalytic Converter	1 liter total volume, Pt:Rh loaded. Catalyst is close coupled to the exhaust manifold.

APPENDIX B

Description of Toyota LCS-M Test Vehicle

Vehicle Identification Number:	AT15102264700000
Curb Weight	2015 lbs
Inertia Weight	2250 lbs
Odometer at Delivery	1358 miles
Transmission	Manual, 5 speed
Shift Speed Code	15-25-40-45 mph
Dynamometer Horsepower	8 HP

Engine:

Fuel	M100 neat methanol
Number of Cylinders	4, in-line
Displacement	97 cubic inches
Camshaft	Single, overhead camshaft
Compression Ratio	11.5, pistons with flat heads are used
Combustion Chamber	Wedge shape
Fuel Metering	Electronic port fuel injection
Bore	3.19 inches
Stroke	3.03 inches
Fuel tank	Stainless steel construction, capacity 14.5 gallons
Ignition	Spark ignition; spark plugs are NDW27ESR-U, gapped at .8 mm, torqued to 13 ft-lb. Toyota recommends changing spark plugs after 9,000 miles of vehicle operation