

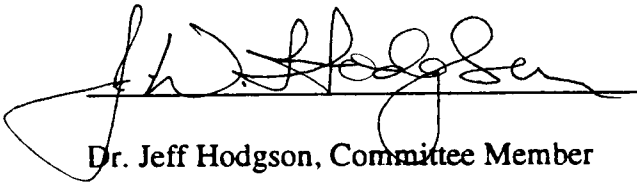
To the Graduate Council:

I am submitting herewith a thesis written by Paul Lisenby entitled "An Experimental Performance Investigation of Natural Gas Catalysts Using a Bench-Flow Reactor". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science, with a major in Mechanical Engineering.



Dr. Ke Nguyen, Major Professor

We have read this thesis  
and recommend its acceptance:



Dr. Jeff Hodgson, Committee Member



Dr. Stan Johnson, Committee Member

Accepted for the Council:



Associate Vice Chancellor  
and the Dean of the Graduate School

**AN EXPERIMENTAL INVESTIGATION OF NATURAL GAS  
CATALYSTS USING A BENCH-FLOW REACTOR**

**A Thesis  
Presented for the  
Master of Science  
Degree  
The University of Tennessee, Knoxville**

**Paul Lisenby  
December 1995**

## DEDICATION

To my wife, *Amy*, with love

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## ABSTRACT

A computer-controlled bench-flow reactor was constructed and used to study the effects of feed stream composition, Pd/Rh loading and washcoat composition on the conversion efficiency of natural gas catalysts. Both fresh and thermally aged catalysts were evaluated using noncycled rich, noncycled lean and cycled stoichiometric feed streams.

Results indicated that the cycled stoichiometric feed stream was the optimum feed stream for effective three-way removal of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO for both the fresh and aged catalysts. In addition, the conversion of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO was found to be maximized with higher Pd/Rh loadings for both the fresh and aged catalysts. By adding ceria to the washcoat, the conversion efficiencies of  $\text{NO}_x$  and CO was enhanced for the fresh catalysts while the conversion of  $\text{CH}_4$  was not affected.

Thermal degradation was found to be a function of Pd/Rh loading on the catalyst, with higher loadings providing a higher degree of resistance to thermal degradation. On the other hand, aged catalysts containing ceria additives were found to degrade considerably which resulted in lower conversion efficiencies for  $\text{CH}_4$ ,  $\text{NO}_x$  and CO as compared to the ceria-free aged catalysts.

It is recommended that further investigations be conducted using dynamometer tests employing a dedicated NGV engine with the catalyst configurations used in this study. In addition, the natural gas catalysts should be evaluated with variable levels of ceria in order to find the level of ceria necessary for an effective oxygen storage capability while providing resistance to thermal degradation.

## TABLE OF CONTENTS

| CHAPTER                                                                                                                | PAGE |
|------------------------------------------------------------------------------------------------------------------------|------|
| 1. INTRODUCTION .....                                                                                                  | 1    |
| 2. LITERATURE REVIEW .....                                                                                             | 5    |
| 2.1 Precious Metals Used in Natural Gas Catalysis .....                                                                | 5    |
| 2.2 Enhanced Catalytic Activity as a Function of Precious Metal Loading .....                                          | 7    |
| 2.3 Effects of Feed Stream Composition on Conversion Efficiencies of CH <sub>4</sub> ,<br>NO <sub>x</sub> and CO ..... | 8    |
| 2.4 Washcoats Used in Natural Gas Catalysts .....                                                                      | 12   |
| 2.5 Aging Effects on Catalyst Performance and Durability .....                                                         | 14   |
| 2.5.1 Thermal Degradation as a Function of Pd/Rh Loading .....                                                         | 15   |
| 2.5.2 Washcoat Effects on Catalyst Durability .....                                                                    | 16   |
| 3. EXPERIMENTAL APPARATUS .....                                                                                        | 17   |
| 3.1 Over-all Description of the Bench-Flow Reactor .....                                                               | 17   |
| 3.2 Experimental Catalysts Used .....                                                                                  | 20   |
| 3.3 Mechanical Components of the Bench-Flow Reactor .....                                                              | 22   |
| 3.3.1 Reactor Test Section .....                                                                                       | 22   |
| 3.3.2 Steam Generator .....                                                                                            | 24   |
| 3.3.3 Water Condenser .....                                                                                            | 27   |
| 3.4 Flow System .....                                                                                                  | 29   |
| 3.4.1 Mass Flow Controllers .....                                                                                      | 29   |
| 3.4.2 Solenoid Valves with Frequency Generator .....                                                                   | 29   |
| 3.4.3 Pressure Transducers .....                                                                                       | 30   |
| 3.4.4 Temperature Sensors .....                                                                                        | 31   |
| 3.4.5 Analyzers .....                                                                                                  | 31   |

|                                                                                                                                                                                     |            |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 3.5 Over-View of Data Acquisition System .....                                                                                                                                      | 32         |
| 3.5.1 Components of the Data Acquisition System .....                                                                                                                               | 35         |
| 3.6 Operation of the Bench-Flow Reactor.....                                                                                                                                        | 39         |
| 3.6.1 Start-up Procedure .....                                                                                                                                                      | 39         |
| 3.6.2 Test Modes .....                                                                                                                                                              | 40         |
| 3.7 Experimental Testing .....                                                                                                                                                      | 41         |
| 3.7.1 Light-off Tests .....                                                                                                                                                         | 41         |
| 3.7.2 Cycled Stoichiometric Light-off Tests .....                                                                                                                                   | 42         |
| 3.7.3 Noncycled Lean Light-off Tests .....                                                                                                                                          | 45         |
| 3.7.4 Noncycled Rich Light-off Tests .....                                                                                                                                          | 45         |
| 3.8 Catalyst Aging Process .....                                                                                                                                                    | 46         |
| <br>4. RESULTS AND DISCUSSION .....                                                                                                                                                 | <br>48     |
| 4.1 Effects of Lean, Rich and Stoichiometric Feed Stream Composition on<br>Conversion Efficiencies and Light-off Temperatures for CH <sub>4</sub> , NO <sub>x</sub><br>and CO ..... | <br><br>48 |
| 4.1.1 CH <sub>4</sub> Conversion .....                                                                                                                                              | 48         |
| 4.1.2 NO <sub>x</sub> Conversion .....                                                                                                                                              | 52         |
| 4.1.3 CO Conversion .....                                                                                                                                                           | 56         |
| 4.2 Effects of Precious Metal Loading on the Conversion Efficiencies and<br>Light-off Temperatures of CH <sub>4</sub> , NO <sub>x</sub> and CO .....                                | <br>59     |
| 4.2.1 Methane Oxidation .....                                                                                                                                                       | 59         |
| 4.2.2 Nitrogen Oxide Reduction .....                                                                                                                                                | 59         |
| 4.2.3 Carbon Monoxide Oxidation .....                                                                                                                                               | 62         |
| 4.2.4 Effects of Loading on the Conversion Efficiencies<br>of CH <sub>4</sub> , NO <sub>x</sub> and CO .....                                                                        | <br>62     |

|                                                                                                                                                 |     |
|-------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.3 Effects of Washcoat Composition on Conversion Efficiencies and Light-off<br>Temperatures for CH <sub>4</sub> , NO <sub>x</sub> and CO ..... | 64  |
| 4.3.1 Methane Oxidation as a Function of Washcoat .....                                                                                         | 65  |
| 4.3.2 NO <sub>x</sub> Reduction .....                                                                                                           | 70  |
| 4.3.3 CO Oxidation .....                                                                                                                        | 70  |
| 4.4 Methane's Complete Oxidation Process in Natural Gas Catalysis .....                                                                         | 74  |
| 4.5 Effects of the Water-Gas Shift Reaction and Steam Reforming Reaction<br>on Carbon Monoxide and Methane Conversion Efficiencies.....         | 77  |
| 4.6 Effects of Aging on Catalyst Performance and Durability .....                                                                               | 78  |
| 4.6.1 CH <sub>4</sub> Conversion Efficiency as a Function of Loading and<br>Washcoat .....                                                      | 80  |
| 4.6.2 NO <sub>x</sub> Conversion Efficiency as a Function of Loading and<br>Washcoat .....                                                      | 87  |
| 4.6.3 CO Conversion Efficiency as a Function of Loading and<br>Washcoat .....                                                                   | 91  |
| 4.7 Explanation of Aging Effects on Loading and Washcoat .....                                                                                  | 93  |
| 5. CONCLUSIONS AND RECOMMENDATIONS .....                                                                                                        | 97  |
| REFERENCES .....                                                                                                                                | 99  |
| APPENDIX .....                                                                                                                                  | 103 |
| VITA .....                                                                                                                                      | 138 |

## LIST OF TABLES

| TABLE                                                | PAGE |
|------------------------------------------------------|------|
| Table I. Catalysts Samples .....                     | 22   |
| Table II. Cycled Stoichiometric NGV Simulation ..... | 43   |
| Table III. Noncycled Lean NGV Simulation .....       | 45   |
| Table IV. Noncycled Rich NGV Simulation .....        | 46   |
| Table V. Catalyst Aging Process .....                | 47   |

## APPENDIX TABLES

|                                                  |     |
|--------------------------------------------------|-----|
| Table A-1 Specifications for the Analyzers ..... | 136 |
| Table A-2 Channel Listings .....                 | 137 |

## LIST OF FIGURES

| FIGURE                                                                                                                                                                                                                                                                 | PAGE |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 1. Oxidation of Methane under Rich Conditions .....                                                                                                                                                                                                                    | 10   |
| 2. Schematic of the Bench-Flow Reactor System .....                                                                                                                                                                                                                    | 18   |
| 3. Photograph of the Bench-Flow Reactor .....                                                                                                                                                                                                                          | 21   |
| 4. Reactor Test Section .....                                                                                                                                                                                                                                          | 23   |
| 5. Steam Generator .....                                                                                                                                                                                                                                               | 26   |
| 6. Water Condenser .....                                                                                                                                                                                                                                               | 28   |
| 7. Schematic Diagram of Interface between PC and Bench-Flow Reactor .....                                                                                                                                                                                              | 34   |
| 8. Bench-Flow Reactor Precatalyst Sampling .....                                                                                                                                                                                                                       | 40   |
| 9. Bench-Flow Reactor Post-catalyst Sampling .....                                                                                                                                                                                                                     | 41   |
| 10. Bench-Flow Reactor Calibration Gas Sampling .....                                                                                                                                                                                                                  | 41   |
| 11. CH <sub>4</sub> Conversion Efficiencies for a Fresh Catalyst with a 60 g/ft <sup>3</sup> Pd/Rh loading<br>and a Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in Rich, Lean and Stoichiometric Lightoff<br>Tests.....  | 49   |
| 12. NO <sub>x</sub> Conversion Efficiencies for a Fresh Catalyst with a 60 g/ft <sup>3</sup> Pd/Rh loading<br>and a Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in Rich, Lean and Stoichiometric Lightoff<br>Tests ..... | 53   |
| 13. CO Conversion Efficiencies for a Fresh Catalyst with a 60 g/ft <sup>3</sup> Pd/Rh loading<br>and a Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in Rich, Lean and Stoichiometric Lightoff<br>Tests .....              | 57   |
| 14. CH <sub>4</sub> Conversion Efficiencies for a Fresh Catalyst with a Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub><br>washcoat in a Stoichiometric Cycled Lightoff Test .....                                                    | 60   |
| 15. NO <sub>x</sub> Conversion Efficiencies for a Fresh Catalyst with a Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub><br>washcoat in a Stoichiometric Cycled Lightoff Test .....                                                    | 61   |

|                                                                                                                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 16. CO Conversion Efficiencies for a Fresh Catalyst with a $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ washcoat in a Stoichiometric Cycled Lightoff Test .....                                                                                          | 63 |
| 17. Palladium and Rhodium Loading on Catalyst Substrate .....                                                                                                                                                                                                          | 64 |
| 18. $\text{CH}_4$ Conversion Efficiencies for Fresh Catalysts with 60 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoat in a Noncycled Lean Lightoff Test .....  | 66 |
| 19. $\text{CH}_4$ Conversion Efficiencies for Fresh Catalysts with 60 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoats in a Noncycled Rich Lightoff Test.....  | 67 |
| 20. $\text{CH}_4$ Conversion Efficiencies for Fresh Catalysts with 60 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ washcoats in a Cycled Stoich. Lightoff Test ..... | 68 |
| 21. $\text{NO}_x$ Conversion Efficiencies for Fresh Catalysts with 10 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoats in a Cycled Stoich. Lightoff Test ..... | 71 |
| 22. CO Conversion Efficiencies for Fresh Catalysts with 40 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoats in a Cycled Stoich. Lightoff Test .....            | 73 |
| 23. CO Conversion Efficiencies for Fresh Catalysts with 60 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$ or $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoats in Noncycled Rich Lightoff Tests .....             | 75 |
| 24. Oxidation of Methane under Rich Conditions .....                                                                                                                                                                                                                   | 76 |
| 25. $\text{CH}_4$ Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 $\text{g/ft}^3$ Pd/Rh loadings and $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$ washcoats in Cycled Stoich. Lightoff Tests .....                                                | 81 |

|                                                                                                                                                                                                                                                                                                                              |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 26. CH <sub>4</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft <sup>3</sup><br>Pd/Rh loadings and Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoats in Noncycled Rich Lightoff<br>Tests .....                                                                           | 82 |
| 27. CH <sub>4</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft <sup>3</sup><br>Pd/Rh loadings and Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoats in Noncycled Lean Lightoff<br>Tests .....                                                                           | 84 |
| 28. CH <sub>4</sub> Conversion Efficiencies for Aged Catalysts with 60 g/ft <sup>3</sup> Pd/Rh loadings<br>and Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> or Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a Noncycled Rich<br>Lightoff Test .....        | 86 |
| 29. NO <sub>x</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft <sup>3</sup><br>Pd/Rh loadings and Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoats in Noncycled Rich Lightoff<br>Tests .....                                                                           | 88 |
| 30. NO <sub>x</sub> Conversion Efficiencies for Aged Catalysts with 10 and 60 g/ft <sup>3</sup> Pd/Rh<br>loadings and Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> or Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a Cycled<br>Stoich. Lightoff Test ..... | 90 |
| 31. CO Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft <sup>3</sup><br>Pd/Rh loadings and Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoats in Noncycled Rich<br>Lightoff Tests .....                                                                      | 92 |
| 32. CO Conversion Efficiencies for Aged Catalysts with 10 and 60 g/ft <sup>3</sup> Pd/Rh<br>loadings and Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> or Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoats in Noncycled Rich<br>Lightoff Tests .....              | 94 |
| 33. Fresh versus Aged Catalyst Comparison .....                                                                                                                                                                                                                                                                              | 96 |

## APPENDIX FIGURES

|                                                                                                                                                                                                                                                                      |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A-1. Top View of Control Board .....                                                                                                                                                                                                                                 | 104 |
| A-2. Electrical Connections of a Typical Mass Flow Controller .....                                                                                                                                                                                                  | 105 |
| A-3. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 106 |
| A-4. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 107 |
| A-5. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 108 |
| A-6. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 109 |
| A-7. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 110 |
| A-8. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 111 |
| A-9. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test .....   | 112 |

|                                                                                                                                                                                                                                                                                         |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A-10. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test .....                     | 113 |
| A-11. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test .....            | 114 |
| A-12. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 115 |
| A-13. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 116 |
| A-14. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test ..... | 117 |
| A-15. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 118 |
| A-16. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 119 |
| A-17. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test ..... | 120 |

|                                                                                                                                                                                                                                                                                                |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A-18. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test ..... | 121 |
| A-19. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 40 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test ..... | 122 |
| A-20. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for a Fresh Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test ..... | 123 |
| A-21. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test .....                          | 124 |
| A-22. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test .....                          | 125 |
| A-23. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test .....                          | 126 |
| A-24. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test .....                          | 127 |
| A-25. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test .....                   | 128 |

|                                                                                                                                                                                                                                                                                                |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A-26. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test .....                            | 129 |
| A-27. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test .....        | 130 |
| A-28. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Lean Noncycled Lightoff Test .....        | 131 |
| A-29. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test .....        | 132 |
| A-30. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Rich Noncycled Lightoff Test .....        | 133 |
| A-31. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 60 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test ..... | 134 |
| A-32. Conversion Efficiencies of CH <sub>4</sub> , NO <sub>x</sub> and CO for an Aged Catalyst<br>with a 10 g/ft <sup>3</sup> Pd/Rh loading and an Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> washcoat in a<br>Stoichiometric Cycled Lightoff Test ..... | 135 |

## LIST OF SYMBOLS

|                                |       |                             |
|--------------------------------|-------|-----------------------------|
| A/D                            | ..... | analog to digital           |
| Al <sub>2</sub> O <sub>3</sub> | ..... | alumina                     |
| °C                             | ..... | degrees Celsius             |
| °C/min                         | ..... | degrees Celsius per minute  |
| C <sub>3</sub> H <sub>6</sub>  | ..... | polypropylene               |
| cc/min                         | ..... | cubic centimeter per minute |
| CeO <sub>2</sub>               | ..... | ceria                       |
| CH <sub>2</sub>                | ..... | methylene                   |
| CH <sub>3</sub>                | ..... | methyl                      |
| CH <sub>4</sub>                | ..... | methane                     |
| cm                             | ..... | centimeter                  |
| cm <sub>2</sub>                | ..... | centimeter squared          |
| CNG                            | ..... | compressed natural gas      |
| CO                             | ..... | carbon monoxide             |
| CO <sub>2</sub>                | ..... | carbon dioxide              |
| D/A                            | ..... | digital to analog           |
| DC                             | ..... | direct current              |
| EGO                            | ..... | exhaust gas oxygen          |
| FC                             | ..... | flow controller             |
| H                              | ..... | hydrogen atom               |
| H <sub>2</sub>                 | ..... | hydrogen molecule           |
| H <sub>2</sub> O               | ..... | water vapor                 |
| HC                             | ..... | hydrocarbon                 |
| HCHO                           | ..... | formaldehyde                |
| hr <sup>-1</sup>               | ..... | per hour                    |

|                                |                           |
|--------------------------------|---------------------------|
| Hz                             | .....Hertz                |
| I.C.                           | .....internal combustion  |
| g/ft <sup>3</sup>              | .....grams per foot cubed |
| LA <sub>2</sub> O <sub>3</sub> | .....Lanthana             |
| mm                             | .....millimeter           |
| min.                           | .....minute               |
| N <sub>2</sub>                 | .....nitrogen molecule    |
| NGV                            | .....natural gas vehicle  |
| NO                             | .....nitrogen oxide       |
| NO <sub>x</sub>                | .....nitrogen oxides      |
| O                              | .....oxygen atom          |
| O <sub>2</sub>                 | .....oxygen molecule      |
| O.D.                           | .....outside diameter     |
| P <sub>1</sub>                 | .....system pressure      |
| P <sub>2</sub>                 | .....vent pressure        |
| P <sub>3</sub>                 | .....vent pressure        |
| P <sub>4</sub>                 | .....analyzer pressure    |
| PC                             | .....personal computer    |
| Pd                             | .....palladium            |
| ppm                            | .....parts per million    |
| Pt                             | .....platinum             |
| R                              | .....redox ratio          |
| Rh                             | .....rhodium              |
| SO <sub>2</sub>                | .....sulfur dioxide       |
| Stoich.                        | .....stoichiometric       |
| THC                            | .....total hydrocarbons   |

TM .....trade mark

V .....volt

# CHAPTER 1

## INTRODUCTION

In today's world of internal combustion engines, the quest for cleaner air has gained momentum in the last few decades of this century. More emphasis has been placed on various alternatives to meet the rising air pollution problems throughout the world. The United States has led the way in this effort by passing stringent clean air regulation and guidelines such as the U.S. Clean Air Act of 1990 and the Energy Policy Act as part of the U.S. National Energy Strategy [1,2,3]\*. To meet this clean air legislation, some approaches to developing alternative sources of power include cleaner fuels and alternative engines, as well as bold proposals such as electric vehicles or utilizing hydrogen as a fuel.

One approach to developing a timely and economically appealing solution is the use of natural gas as an alternative fuel. The interest in natural gas stems from its ample availability, vast reserves, competitive price advantage and cleaner burning capability over gasoline [4,5]. Natural gas, which consists primarily of methane (85-95% of the total hydrocarbons), has excellent knock resistance and flammability over a wide range of air-fuel ratios [2]. Natural gas is also an excellent fuel for Otto-cycle (spark-ignition) engines. Since it exists as a gas under normal conditions, it has the potential to mix with air in any proportion, and unlike liquid fuels it does not need to vaporize before it will burn. This characteristic of natural gas allows easier cold engine starting and cold-start enrichment is not required. This cold-start enrichment is a major source of CO emissions and emissions-related problems in gasoline-fueled vehicles [1,6]. Due to the low density of natural gas, a stoichiometric mixture of natural gas occupies about 10% more volume

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\* Numbers in [ ] refer to entries in bibliography.

than a stoichiometric gasoline/air mixture with the same energy content. Therefore, for a fixed engine displacement relative to gasoline/air mixtures, the amount of natural gas/air mixture that can be burned in each cycle is about 10% less, resulting in a lower engine power output. A gasoline engine converted to natural gas will thus produce about 10% less power at full throttle than on gasoline. In dedicated natural gas engines, this can be overcome by increasing the compression ratio. The higher efficiency due to the increased compression ratio results in more work output for each unit of fuel inducted, thus offsetting the reduced maximum induction rate [6]. In addition, compared with gasoline, natural gas's higher octane number and wider flammability limits theoretically enable compressed natural gas (CNG) engines to be operated more efficiently with leaner air-fuel mixtures and higher compression ratios [7,8]. By retrofitting existing engines and the modification of new engines to utilize natural gas as a fuel, an effective method in dealing with rising air pollution can be found.

In the investigation presented herein, experimental studies were conducted on natural gas catalysts exposed to simulated natural gas exhaust streams. Historically, standard dynamometer tests have been used to generate the data required for a complete exhaust analysis. However, these tests resulted in varying degrees of accuracy and repeatability due to the number of variables associated with the internal combustion engine. To circumvent this problem, a bench-flow reactor has been designed and constructed to accurately simulate the exhaust constituents of a CNG engine and achieve the conversion characteristics of a natural gas catalytic converter.

The primary purpose of the bench-flow reactor is the reduction of significant variables of performance associated with the engine and the evaluation of different types of catalysts and their associated performance under similar operating conditions. To achieve this objective, the bench-flow reactor is able to simulate the typical oscillation that occurs about the stoichiometric point during closed-loop operation of the engine, as

well as being able to show various conditions that a catalyst undergoes in real time situations. These situations include the initial cold starting of the engine, the power enrichment that occurs during acceleration, and other subsequent driving conditions.

By using the bench-flow reactor, the performance of three-way natural gas catalysts in the reduction and oxidation of nitrogen oxides ( $\text{NO}_x$ ) carbon monoxide (CO) and methane ( $\text{CH}_4$ ) was investigated by the use of light-off tests. The natural gas catalysts used in this study consisted of palladium and rhodium metals impregnated at different loadings on alumina/lanthana washcoats with and without ceria additions. The performance of these catalysts in response to feed stream composition, palladium/rhodium loadings, ceria washcoat additions and thermal degradation was investigated.

The uniqueness of this investigation into NGV catalysts lies in the types of precious metals employed in conjunction with the washcoat compositions used. Numerous investigations on the effect of palladium/rhodium (Pd/Rh) loadings and alumina/ceria washcoat compositions on the performance of catalysts have been carried by researchers [9,10,11]. However, the simultaneous investigation of these parameters in an NGV simulated environment has not been examined to the author's knowledge. Therefore, this research provides an in-depth look at the interactions of the Pd/Rh metals with alumina/ceria washcoat compositions in terms of catalyst performance during various exhaust stream conditions. In addition, this study investigates the degree of thermal degradation that the catalyst undergoes as a function of the Pd/Rh loading and the addition of ceria to the washcoat. The results of this investigation can be used to better characterize the behavior of NGV catalysts under various conditions and consequently lead to catalyst designs with higher performance capabilities.

Chapter 2 of this thesis presents a literature review of other research efforts that are used to establish viable natural gas catalysts for NGV engines. In Chapter 3, the

over-all design of the bench-flow reactor, the testing procedures used in the evaluation of the natural gas catalysts, and the specifications of the natural gas catalysts are presented. Chapter 4 discusses the performance of the natural gas catalysts under noncycled lean, noncycled rich and cycled stoichiometric operating conditions in regards to Pd/Rh loadings, washcoat compositions and thermal degradation. Finally, Chapter 5 gives the conclusions gained from this research effort and presents the recommendations for future studies on natural gas catalysts.

## CHAPTER 2

### LITERATURE REVIEW

The purpose of this chapter is to present a summary of past investigations on the design and testing of natural gas catalysts. Section 2.1 provides an introduction to the types of precious metals used in natural gas catalytic converters and the advantages associated with each type. Section 2.2 provides the correlation of the amount of precious metals used in regards to increased catalytic activity. Section 2.3 provides a look at the research efforts used to determine the effects of the feed stream composition on the conversion efficiencies of  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{NO}_x$ . Research investigations on the performance of catalyst containing alumina washcoats with and without the addition of cerium oxide are investigated in Section 2.4. Finally, Section 2.5 presents research investigations into the thermal degradation of the catalyst in regards to the amount of palladium/rhodium metals present on the catalyst and the thermal degradation associated with cerium oxide additions to the washcoat.

#### 2.1 Precious Metals used in Natural Gas Catalysis

Some of the most common noble metals used in current catalyst configurations are platinum (Pt), palladium (Pd), and rhodium (Rh). The amount of loading of these metals onto the catalyst is an important cost consideration to catalyst manufacturers due to their limited availability. For instance, the current usage level of rhodium in automobile catalytic converters is significantly higher than the mining rate, which raises serious concern over its price and availability in the future [9]. Therefore, extensive research efforts have been geared toward reduction or elimination of the rhodium requirement in three-way catalytic converters without adversely affecting the overall

converter performance. However, research conducted by Cho [9] indicates that among the major ingredients of three-way catalyst, rhodium is superior for nitric oxide reduction, as well as carbon monoxide oxidation compared with platinum or palladium.

The oxidation of  $\text{CH}_4$  is also a primary concern since the stability of this constituent makes it the most difficult of all hydrocarbons to oxidize catalytically. Research findings by Oh, Mitchell and Siewert [10] suggest that palladium catalysts are typically more active than platinum and rhodium catalysts for  $\text{CH}_4$  oxidation. An important side benefit to this higher reactivity of palladium is that the cost of palladium is less than either platinum or rhodium, so it is not only a preferred solution to the reduction of  $\text{CH}_4$  in NGV exhaust, but it is also a cost-effective resolution.

To further examine the effect of precious metal loading, Oh, Mitchell and Siewert [10] conducted experimental investigations on methane's oxidation activity over alumina-supported palladium, platinum and rhodium catalysts. They observed that under net-oxidizing and net-reducing feed stream conditions, all of the catalysts promoted either complete or partial oxidation of methane to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , with an activity ranking of  $\text{Pd} > \text{Pt} > \text{Rh}$ . The net-oxidizing condition refers to a fuel lean bias where the ratio of the air to the fuel (A/F ratio) present in the feed stream is greater than under stoichiometric conditions. Similarly, the net-reducing condition refers to a fuel rich bias, where the air to fuel ratio is less than seen for stoichiometric conditions.

From the experimental findings of researchers like Cho [9] and Oh et al. [10] the combination of palladium and rhodium in natural gas catalysts yields not only the effective reduction of NO and the oxidation of CO by rhodium, but also the superior oxidation of  $\text{CH}_4$  by palladium. Therefore, Pd/Rh catalysts are found to provide exceptional conversion results in the catalysis of natural gas above all other combinations of platinum, palladium and rhodium catalysts.

## 2.2 Enhanced Catalytic Activity as a Function of Precious Metal Loading

As mentioned previously, the amount of the precious metal loading is of primary importance in the cost consideration for developing natural gas catalysts. Therefore, current research has been focused on minimizing the amount of precious metal loading on the catalysts while still meeting federal guidelines. Consequently, research has been focused on determining the effect of increased precious metal loading on the conversion efficiencies of methane, nitrogen oxides and carbon monoxide in exhaust emissions. One such study was undertaken by Usmen et al. [11] in the design of an effective natural gas catalytic converter. In their study, they conducted bench-flow reactor experiments to investigate the effects of the operating temperature and the amount of palladium loading on the performance of catalysts under simulated natural gas vehicle exhaust conditions. By using palladium loadings of 40 g/ft<sup>3</sup> and 120 g/ft<sup>3</sup>, they discovered that higher loadings of palladium resulted in a much lower CH<sub>4</sub> light-off temperature in comparison with the lower loading.

Similar research was conducted by Williamson, Summers and Skowron [12] on the effects of rhodium loading on the conversion efficiencies of NO<sub>x</sub> and CO in the feed stream. Their research was conducted by using standard dynamometer tests using a Nissan 300ZX vehicle and Pt/Rh catalysts. They found that the conversion of NO<sub>x</sub> and CO conversion increased up to 15% when the rhodium content was increased from 4.5 g/ft<sup>3</sup> to 8.5 g/ft<sup>3</sup>. The amount of rhodium in the catalyst was increased by increasing the Pt/Rh ratio from 10:1 to 5:1 at the same loading level.

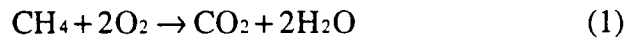
### 2.3 Effects of Feed Stream Composition on Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO

The conversion efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO are directly related to the feed stream composition. This correlation has been extensively investigated by researchers in order to determine an optimum operating point for NGV engines.

One such investigation was conducted by Subramanian, Kudia and Chattha [13]. The objective of their study was to investigate the modes of methane removal from simulated CNG fueled exhaust under net-oxidizing, net-reducing and stoichiometric conditions. Model reactions studies were conducted for the natural gas simulation using palladium catalysts supported by an alumina (Al<sub>2</sub>O<sub>3</sub>) washcoat.

Based on the results they concluded that maximum CH<sub>4</sub> conversion efficiencies were achieved during a stoichiometric natural gas simulation when compared with rich and lean feed streams. In addition, the rich (or net-reducing) feed stream simulation provided superior conversion efficiencies when compared to the lean or net-oxidizing feed stream.

The study suggested that the CH<sub>4</sub>-O<sub>2</sub> reaction described in equation (1)



contributes to the removal of methane under net-oxidizing conditions. Whereas, under net-reducing feed streams, the oxidation of methane occurred not only by the CH<sub>4</sub>-O<sub>2</sub> reaction shown in equation (1), but also by the CH<sub>4</sub>-NO reducing reaction shown in equation (2) which was consistent with conclusions made by Usmen et al. [11].



The experimental results of Subramanian, Kudia and Chattha were also consistent those obtained by Oh, Mitchell and Siewert [10] for the methane oxidation activity in net-oxidizing, net-reducing, and stoichiometric environments. Oh et al. conducted bench-flow reactor studies with varying degrees of air/fuel bias at a fixed temperature to determine the

corresponding effects on methane conversion. To study the effect on methane oxidation,  $\text{CH}_4$ -CO- $\text{O}_2$  mixtures containing 0.2 vol%  $\text{CH}_4$ , 0.1 vol% CO, (0.33-1) vol%  $\text{O}_2$  and a balance of nitrogen were used.

For the oxidation of methane, the results suggested that maximum conversion of methane occurs at feed stream slightly richer than stoichiometric. In addition, net-reducing conditions were favored for methane conversion than the net-oxidizing conditions. Oh, Mitchell and Siewert suggested that the reason for the lower methane conversion in the net-oxidizing feed stream was due to the noble metal surface being predominantly covered with oxygen. As a result, the critical step in the methane dissociative adsorption on the catalyst surface was effectively blocked by the oxygen molecules.

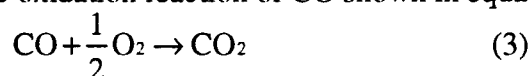
Oh, Mitchell and Siewert concluded that most kinetic studies conducted over noble metal catalysts in the presence of excess  $\text{O}_2$  show that the observed rate law is first order in methane and zero order in oxygen. In addition, oxygen adsorption on noble metals has been shown to be fast under net-oxidizing conditions whereas methane adsorption is a slow process. As a result of the substantial difference in adsorption strengths,  $\text{O}_2$  acted as an inhibitor for  $\text{CH}_4$  oxidation under the net-oxidizing environment by excluding the more weakly adsorbed species,  $\text{CH}_4$ , from the active sites. In addition, they surmised that the reason for the superior oxidation activity under net-reducing feed streams was a result of methane's ability to compete successfully for active sites despite its weaker adsorption strength. Consequently, in the slightly rich feed stream, the adsorption rates for the  $\text{CH}_4$  and  $\text{O}_2$  are comparable and thus higher  $\text{CH}_4$  conversions result.

In this study Oh, Mitchell and Siewert also proposed methane's complete oxidation process in a natural gas simulation under net-reducing, or rich, conditions as shown in Figure 1.

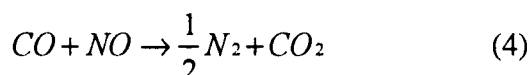


closed-loop emission control systems as a result of the (EGO), exhaust gas oxygen, sensor. These fluctuations of the exhaust composition occur on both the lean and rich side of stoichiometric. Consequently, it is of practical interest to understand the kinetic behavior of the CO + NO reaction under these cycled feed stream conditions as well as under steady-state conditions.

One such study that investigated the conversion characteristics of NO and CO as a function of the feed stream composition was undertaken by Oh and Carpenter [14]. The objective of their study was to determine the reactions of CO with O<sub>2</sub> and NO over supported noble metal catalysts in lean, rich and stoichiometric environments. Of particular interest to Oh and Carpenter was the inhibiting effect of NO on the rate of the CO-O<sub>2</sub> reaction. In their study, Rh/Al<sub>2</sub>O<sub>3</sub> catalysts were used in a laboratory reactor with CO-NO-O<sub>2</sub> mixtures. By simulating lean, rich and stoichiometric conditions, they found that the rate of the oxidation reaction of CO shown in equation (3) as



was significantly reduced in the presence of NO in the feed stream. In addition, it was found that the oxidation of CO could not occur until the CO-NO reaction shown in equation (4) was significant.



This was due presumably to the adsorbed NO molecules blocking the catalyst's active sites and thus limiting the oxidation of CO. Therefore, they concluded that the oxidation of CO and the reduction of NO in the exhaust stream was primarily determined by the CO-NO reaction as opposed to the CO-O<sub>2</sub> reaction.

## 2.4 Washcoats Used in Natural Gas Catalysts

Another important parameter in the design considerations for natural gas catalysts is the washcoat used on the catalyst substrate. Catalyst substrates, typically cordierite, have very low internal surface area due to their coarse pore structure. A washcoat is used to provide the fine internal pore structure necessary for catalytic activity. Each pore created by the washcoat is called an activation site. The exhaust gas enters the catalyst and is adsorbed onto these activation sites. As a result, these activation sites define the activity of the catalyst for the dissociation of the constituents in the feed stream and consequently the resulting oxidation and reduction reactions of the constituents.

Aluminum oxide,  $Al_2O_3$ , is a common representative of a catalyst washcoat and is currently used extensively in NGV exhaust catalysis. A common additive to the  $Al_2O_3$ , or alumina, washcoat is lanthanum oxide,  $La_2O_3$ . Lanthanum oxide is used to act as a thermal stabilizer to the alumina support [15]. Another type of washcoat is cerium oxide,  $CeO_2$ . As a washcoat cerium oxide, or ceria, has been widely used as an additive ingredient in NGV three-way catalytic converters for various reasons; it promotes the water-gas shift reaction [16,17], it stabilizes the dispersion of noble metals on an alumina support [18], and it stores and releases oxygen under net-oxidizing and net-reducing conditions [16,17]. Even though the oxygen storage capability of ceria has been widely known in automobile exhaust catalysis, the idea of enhancing the catalytic activity of noble metals for NO decomposition by improving the oxygen storage capacity of the support material is relatively new [19].

The effects of the oxidation activity of ceria-promoted noble metal catalysts were investigated by Oh, Mitchell and Siewert [10]. Laboratory reactor studies were conducted to evaluate the steady-state conversions of  $CH_4$  and CO over  $Pt/Al_2O_3$ ,  $Pd/Al_2O_3$  and  $Rh/Al_2O_3$  catalysts with and without the addition of ceria to the washcoat. The results indicated that CO conversion under net-oxidizing conditions was

highest for the Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. In contrast, under similar conditions, the CH<sub>4</sub> oxidation activity of the Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts was significantly less than the CH<sub>4</sub> oxidation activity achieved by the ceria-free catalysts, Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>. In addition, the ceria-induced suppression of the CH<sub>4</sub> oxidation activity was found to be most dramatic for the Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst which resulted in a light-off temperature increase of 200° C over the ceria-free Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. However, under the net-oxidizing conditions, the activity of the Rh/Al<sub>2</sub>O<sub>3</sub> was found to be virtually unaffected by the ceria addition. Consequently, the activity ranking in the presence of excess O<sub>2</sub> changed from Pd > Rh > Pt without cerium to Rh > Pd ≈ Pt in the presence of ceria. Therefore, Oh, Mitchell and Siewert concluded that the addition of ceria to Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts did result in an increase in CO conversions, but this advantage was offset to some degree by the loss in CH<sub>4</sub> conversion efficiency.

Similar studies by Oh and Eickel [20] have demonstrated the effects of ceria addition on CO oxidation kinetics over alumina-supported rhodium catalysts. They discovered that in strongly oxidizing environments, the rate of CO oxidation was virtually unaffected in the presence of ceria. On the other hand, in moderately oxidizing or net-reducing conditions, the addition of sufficient amounts of ceria to the catalysts resulted in an enhancement of the CO oxidation activity which resulted in superior conversion results compared to the ceria-free catalysts.

Cerium additions to catalysts can also have an effect on the CO-NO reaction kinetics as was seen in a study conducted by Oh [21] involving alumina supported rhodium catalysts. Laboratory reactor studies were conducted in CO-NO feed streams with N<sub>2</sub> as a carrier gas. It was found that there was an enhanced CO-NO reaction rate in the presence of ceria as opposed to the ceria-free Rh/Al<sub>2</sub>O<sub>3</sub> catalysts. In addition, the results generated during these experiments suggested that there was an increase in

activation energy associated with temperature increases for the catalysts with the ceria additive. In contrast, the cerium-free alumina washcoats were observed to have an apparent constant activation energy even at elevated temperatures. Furthermore, Oh theorized that the mechanism by which ceria promoted the increased NO dissociation was due to the formation of ceria islands on the catalyst surface. The NO adsorbed in such a fashion that the nitrogen end of the molecule was attached to the rhodium metal and the oxygen end to an oxygen-deficient cerium species, CeO. The interaction of both ends of the NO molecule weakened the N-O bond and thereby resulted in a higher dissociative reaction rate as compared to the ceria-free catalysts.

## **2.5 Aging Effects on Catalyst Performance and Durability**

One of the most critical factors in the over-all effectiveness of a catalyst is its ability to resist the effects of thermal degradation. The stability of methane in the feed stream requires elevated catalyst operating temperatures in order to ensure the oxidation reaction of CH<sub>4</sub>. Therefore, current NGV exhaust designs prescribe the location of the catalytic converter much closer to the exhaust manifold than in gasoline vehicle exhaust configurations. Therefore, the ability of the catalyst to withstand high temperatures becomes a critical factor in the performance of the catalyst. Moreover, the proposed requirement for automobile catalysts to reduce vehicle emissions to within legislated standards over 100,000 miles also places an emphasis on the rate of catalyst deactivation during use [32].

The durability and degree of degradation of the catalyst can be a function of several parameters such as the type of precious metal loading on the catalyst, the amount of loading, and the type of washcoat chosen. The effects of each of these parameters is currently under extensive investigations to determine the best combinations of parameters capable of yielding superior catalyst conversion capabilities over the life of the catalyst.

Another potential problem is the thermal interaction of these parameters, such as the precious metal with the catalyst washcoat, that lead to undesirable formations that result in a reduction of catalytic activity. To understand this loss of conversion capability, catalyst designers are currently devising catalyst configurations through planned experimentation to reveal the interactions that lead to thermal deactivation. Some of the processes leading to thermal deactivation that have been discovered include: 1) the loss of active noble metal surface area through sintering, 2) undesirable interactions of the noble metals with the washcoat, 3) the formation of less active noble metal alloys, and 4) the loss of the washcoat surface area through sintering or chemical phase change [9].

### **2.5.1 Thermal Degradation as a Function of Pd/Rh Loading**

The effect of precious metal loading in regards to thermal stability was investigated by Muraki and Sobukawa [22]. In this study, Pd/Rh catalysts with a palladium to rhodium ratio of 5:1 were used in a laboratory reactor to determine the effect of loading on catalyst durability. Pd/Rh loadings of 20, 40 and 50 g/ft<sup>3</sup> were used and the catalysts were aged at temperatures between 700° C to 800° C while being exposed to the exhaust of a 2.8 liter, gasoline engine operating under steady-state conditions at a stoichiometric air/fuel ratio. The total hydrocarbons, THC, nitrogen oxides and carbon monoxide constituents present in the exhaust stream were measured during the testing process. The aging process time duration was 30 hours.

The results of the Pd/Rh loadings on the stoichiometric light-off performance of the catalysts clearly demonstrated the effect of precious metal loadings on catalyst durability in the aging process. As the loading increased, the light-off temperature for the THC, CO and NO<sub>x</sub> decreased. Therefore, Muraki et al. concluded that higher Pd/Rh loadings were desired for increased catalyst durability in order to achieve acceptable levels of THC, NO<sub>x</sub> and CO conversions over the life of the catalyst.

### 2.5.2 Washcoat Effects on Catalyst Durability

Theis, Casarella and Mahan [23] investigated the effect of ceria additives on the durability of three-way catalysts. Of particular interest to them was whether or not the added benefits of ceria were still present after aging. In their study, aged catalyst were used with the same noble metal loading of 0.14 wt.% Pt and 0.14 wt.% Rh but with varying levels of ceria from 0 to 50 wt.%. The results of the experiment indicated that the catalysts containing ceria were subject to a high degree of thermal deactivation when exposed to high temperatures. In addition, it was found that the oxygen-storage capacity advantage of the ceria additive was virtually lost after experiencing aging temperatures at or above 800° C. The interaction of the ceria particles and the noble metals present resulted in a chemically deactivating process. Furthermore, the results indicated that the hydrocarbon conversion efficiency was less dependent on the oxygen/storage release component as compared to the CO present in the feed stream. Theis, Casarella and Mahan suggested that this was due in a large part to the fact that during rich exhaust streams hydrocarbon conversions occur through reactions other than oxidation by O<sub>2</sub>.

## CHAPTER 3

### EXPERIMENTAL APPARATUS

This chapter describes the experimental apparatus, the testing procedures and the catalysts used in the present investigation. Section 3.1 provides an over-all description of the bench-flow reactor. The natural gas catalysts used in the present study are described in Section 3.2. Section 3.3 focuses on the mechanical components of the bench-flow reactor while Section 3.4 provides the description of the flow system and analyzers used. The design and operation of the computer-controlled data acquisition system for the bench-flow reactor is described in Section 3.5, and Section 3.6 provides the operating instructions for the start-up of the bench-flow reactor. In Section 3.7, the experimental testing used for the simulation of NGV exhaust is shown and Section 3.8 discusses the aging process used for the catalysts.

#### 3.1 Over-all Description of the Bench-Flow Reactor

A schematic of the bench-flow reactor is shown in Figure 2. Simulated NGV exhaust gases are introduced into the bench-flow reactor via mass flow controllers. These gases consist of CO, NO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. Water vapor is introduced into the system by a steam generator. The methane constituent, CH<sub>4</sub>, is a common representative of the hydrocarbon species prevalent in natural gas; however, with other types of hydrocarbon fuels such as gasoline, this constituent can be replaced by polypropylene (C<sub>3</sub>H<sub>6</sub>) as the hydrocarbon species. In addition, if a gasoline simulation is desired, the bench-flow reactor has the capability of injecting SO<sub>2</sub> in the feed stream to accurately reflect the exhaust constituents from a gasoline engine.

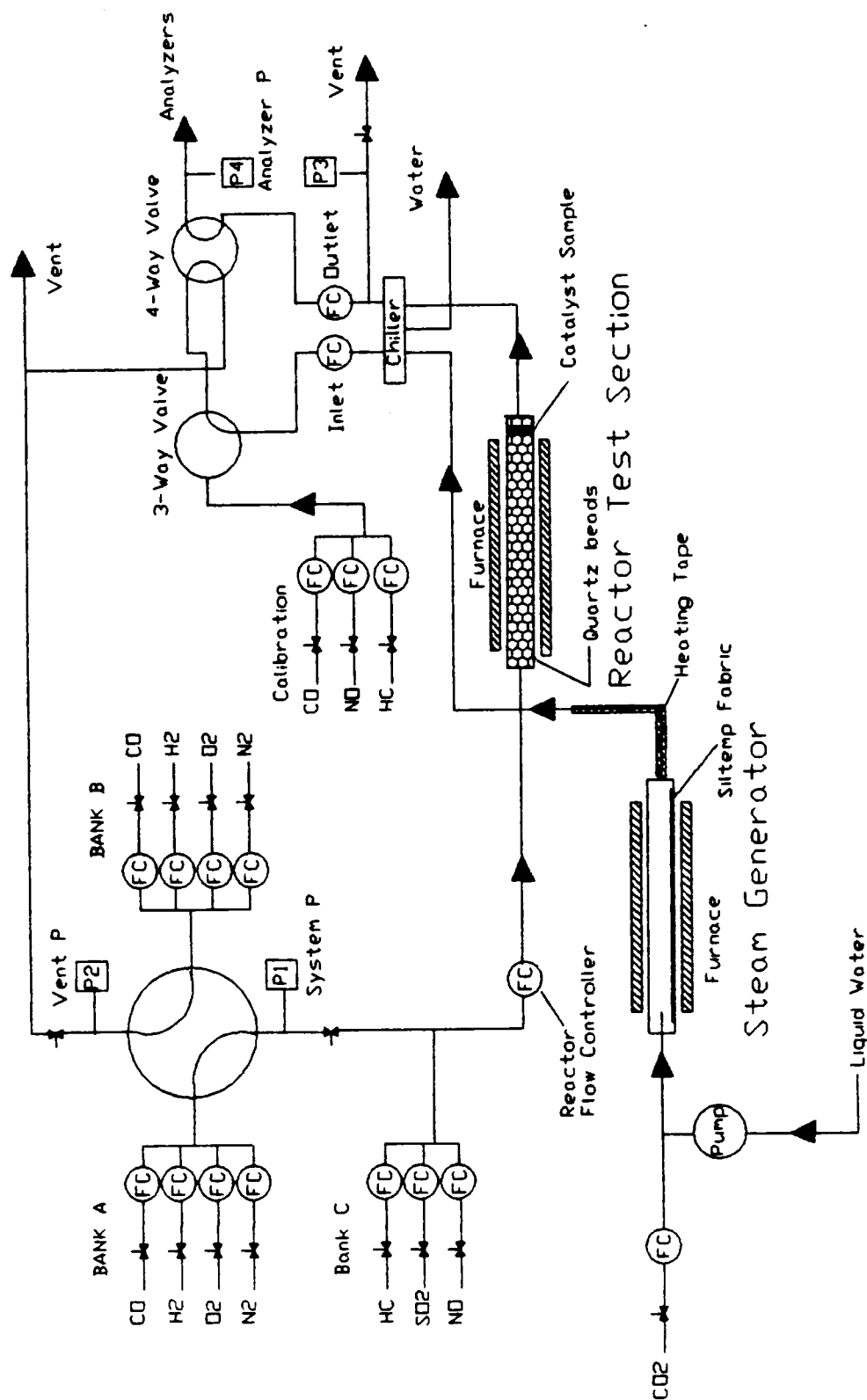


Figure 2: Schematic of the Bench-Flow Reactor System

In order to simulate the typical oscillation about the stoichiometric operating point in real engines, the bench-flow reactor is equipped with solenoid valves. This stoichiometric oscillation can be described as fuel rich or fuel lean pulses that are a direct result of the Exhaust Gas Oxygen (EGO) sensor's effort to operate the engine in the stoichiometric window. Furthermore, to simulate the typical temperature extremes experienced by the catalyst in the catalytic converter, the bench-flow reactor is equipped with a laboratory reactor test section. In this test section, the catalyst is placed inside of a quartz tube and heated by the reactor furnace to the desired exhaust temperatures. Thermocouples placed on both ends of the catalyst in the test section allow a direct correlation between the catalyst temperature and the corresponding oxidation or reduction of the constituents in the feed stream.

In order to simulate the water vapor that occurs in typical NGV exhaust, a steam generator capable of supplying a constant flow rate of steam is used. For a dry-gas analysis to be conducted on the exhaust gases, a condenser is employed to condense and remove water vapor from the gas mixture. The removal of the water vapor after catalysis and before the analyzers is required to ensure that the analyzers are protected from possible water damage.

By using three-way and four-way valves, the bench-flow reactor can be operated in different modes. The first mode consists of utilizing a by-pass valve so that the blended exhaust gases in the feed stream can flow to the emission analyzers before they pass over the catalyst sample. This mode is referred to as the pre-catalyst mode and is used to determine the composition of the constituents in the feed stream prior to catalysis. The second mode, or post-catalyst mode, analyzes the exhaust gases after catalysis. The combination of mode 1 and mode 2 allows a direct composition comparison of the constituents before and after catalysis to determine the resulting conversion efficiencies of the gases across the catalyst. Finally, a calibration gas bank

can be sampled during the testing process to ensure the ongoing accuracy of the gas analyzers.

In order to create an environment with a high degree of accuracy, the bench-flow reactor is equipped with a computer-controlled laboratory reactor system. This system has the capability of controlling the furnace of the reactor system so that light-off and sweep test can be conducted. The system is also able to control the mass flow rates of the gases entering the system such that lean, rich and stoichiometric conditions can be simulated. As a result of these conditions, the simulated NGV exhaust can be studied with a varying degree of net-oxygen or air/fuel bias. This computer-control technique is accomplished via A/D converter boards interfaced between the bench-flow reactor and the computer. The following portions of this chapter deal with defining and discussing each component of the bench flow reactor and their contribution in the testing procedure. A photograph of the bench-flow reactor can be seen in Figure 3.

### **3.2 Experimental Catalysts Used**

The ten monolith catalysts chosen for this experiment were supplied by United Emission Catalyst. Each of these catalysts have a cordierite substrate support, cell density of 400 cells/in<sup>2</sup>, and Pd/Rh precious metals loaded on to the catalysts at a 5:1 ratio. In order to evaluate the performance of these catalysts in regards to loading, the Pd/Rh metals are impregnated onto the catalysts at three different loadings: 10, 40 and 60 g/ft<sup>3</sup>. In addition, the catalysts are investigated based on the washcoat configuration. Six of the catalyst samples contain an alumina, Al<sub>2</sub>O<sub>3</sub>, and lanthana, La<sub>2</sub>O<sub>3</sub>, washcoat while the other six contain the alumina/lanthana washcoat with the addition of ceria, CeO<sub>2</sub>. The catalysts containing the Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat have an average washcoat weight of 24% of the total loaded weight, including the Pd/Rh loadings, with 98% of the

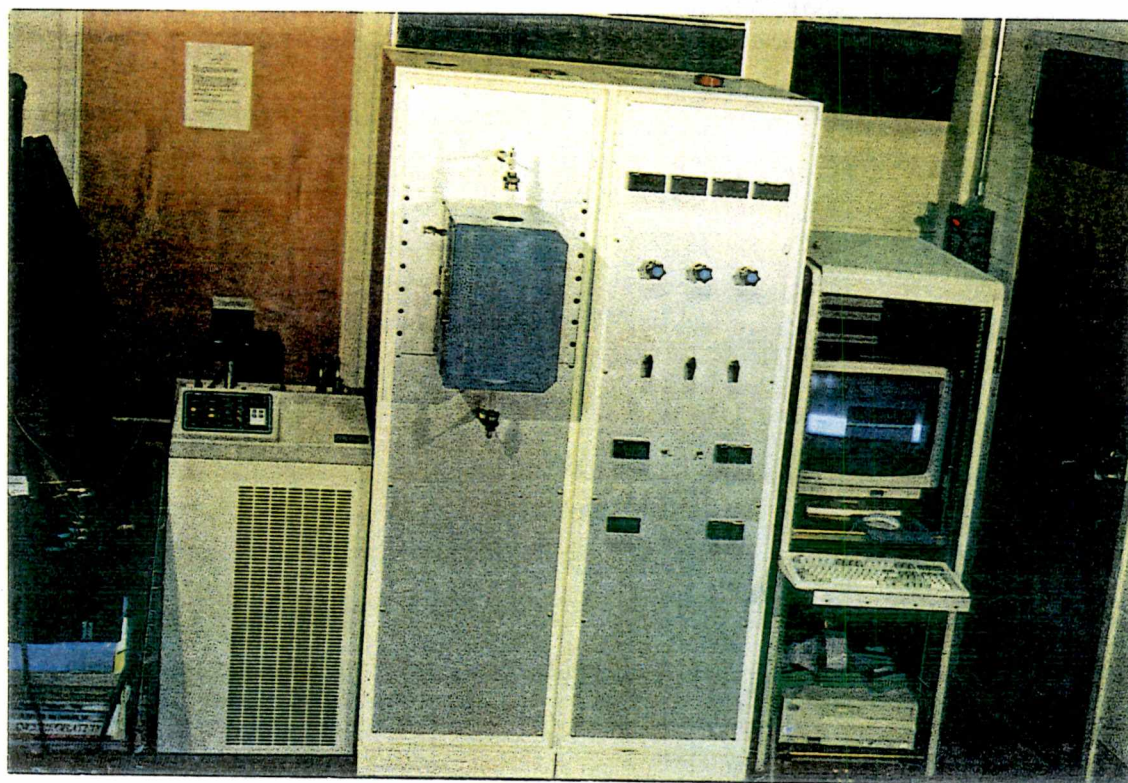


Figure 3: Photograph of the Bench-Flow Reactor

washcoat alumina and 2% lanthana. The catalysts with the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$  washcoat have an average washcoat weight of 26% of the total weight with 78% of the washcoat alumina, 20% of the washcoat ceria and the remaining 2% lanthana. The catalysts used in this study are shown in Table I.

Table I. Catalysts Samples

| Number | Condition | Loading           | Washcoat                                                   |
|--------|-----------|-------------------|------------------------------------------------------------|
|        |           | g/ft <sup>3</sup> |                                                            |
| 1      | Fresh     | 60                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$              |
| 2      | Fresh     | 40                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$              |
| 3      | Fresh     | 10                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$              |
| 4      | Aged      | 60                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$              |
| 5      | Aged      | 10                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$              |
| 6      | Fresh     | 60                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$ |
| 7      | Fresh     | 40                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$ |
| 8      | Fresh     | 10                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$ |
| 9      | Aged      | 60                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$ |
| 10     | Aged      | 10                | $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{CeO}_2$ |

### 3.3 Mechanical Components of the Bench-Flow Reactor

#### 3.3.1 Reactor Test Section

The reactor test section, shown in Figure 4, consists of a 25-mm diameter, 61-cm long quartz tube. Cajon-type fittings are used on each end of the test section to facilitate reactor installation and removal. The tubular reactor is placed inside a Lindberg Minimate single zone furnace (Model #55035). The quartz tube is filled with quartz beads in order to improve the heat transfer from the furnace to the exhaust gases thereby ensuring a uniform temperature throughout the flow. The quartz beads also prevent mixing

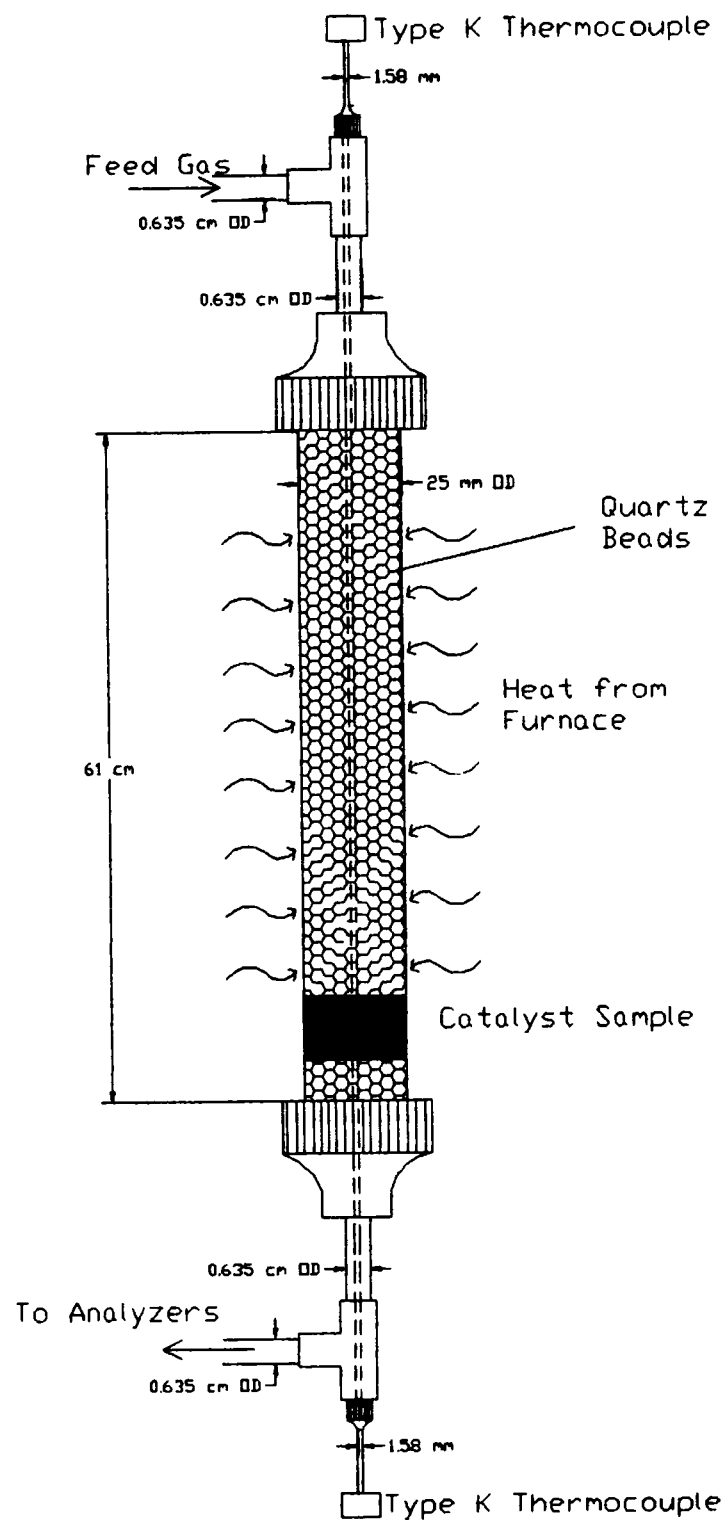


Figure 4: Reactor Test Section

between lean and rich pulses of the gases during cycled testing. A monolith catalyst sample is placed inside the quartz tube and positioned in the downstream section where the quartz tube just emerges out of the furnace casing. The catalyst sample is prepared to obtain a  $1 \text{ cm}^2$  cross-section. By varying the length of the catalyst sample, the desired space velocity ( $\text{hr}^{-1}$ ) through the catalyst and, consequently, the residence time can be controlled. The space velocity is defined as the ratio of the volumetric flow rate of the gases through the catalyst to the void volume of the catalyst sample.

The catalyst sample inside the quartz tube is wrapped in *FiberFrax*<sup>TM</sup> glass wool to ensure that the gas stream passes through the catalyst sample and not around its edges. The reactor furnace is used to heat the gas stream and catalyst sample inside the test section and thereby simulating the hot exhaust gas flow through the catalytic converter in real engines. To allow for better temperature control of the catalyst sample, the Lindberg furnace utilizes an internal type K thermocouple along with a four segment programmable controller capable of delivering two ramp and two dwell heating periods. This aspect of the furnace allows accurate temperature sweeps for the catalyst sample. Any quartz tube surface residing outside of the furnace housing is insulated using glass wool to prevent heat loss to the surroundings. Gas temperatures before and after the catalyst are measured with 1.58 mm O.D., type K thermocouples. These thermocouples are inserted from the top and bottom of the quartz tube by the use of Swagelok fittings until they are just in contact with the catalyst sample. Digital temperature indicators, Omega Model DP41 series, mounted on the control panel are used to monitor the temperature of the sample.

### 3.3.2 Steam Generator

Typical NGV engine exhaust contains a large percentage of water vapor. To simulate this constituent, a steam generator is used to supply superheated steam at a constant mass flow rate without entrained droplets entering the bench-flow reactor at the catalyst site. A schematic of the steam generator is shown in Figure 5. The steam generator system consists of a Lindberg Mini-Mite single zone furnace, a Masterflex peristaltic pump, a 0.6 cm thick strip of Siltemp<sup>TM</sup> fabric, and a quartz tube that has a 25-mm O.D., and is 51.0 cm long. The adjustable peristaltic pump uses a 1.58 mm O.D. maxiflow silicone tubing to inject distilled water at a specified flow rate. The silicone tubing is connected to a 1.58 mm O.D. stainless steel injector at the entrance of the quartz tube. The quartz tube is placed inside of the furnace and heated at a constant temperature of 400° C to ensure adequate temperature for complete steam generation. A thin strip of woven Siltemp<sup>TM</sup> silica fabric with a very high capillary action is placed flat on the bottom of the quartz tube so that its leading end lies in the cold zone outside the furnace, while the majority of the fabric is in the hot region inside the furnace. The purpose of the Siltemp<sup>TM</sup> strip is to act similarly to the wick of an oil lamp. Distilled water from the peristaltic pump is injected at a specified flow rate on the cold region of the strip. The water is then drawn by capillary action into the heated end of the strip, thus giving a uniform flow rate of steam as the water evaporates off the strip of silica fabric. The flow rate of distilled water can be controlled to generate a desired amount of steam entering the system. For example, a typical test run consists of about 0.83 cc/min of liquid water injected by the peristaltic pump which amounts to 1 L/min of steam entering the system.

The resulting water vapor from the steam generator is carried through the system by the introduction of carbon dioxide as a carrier gas at the inlet of the quartz tube. To prevent condensation from occurring in the system before the steam reaches the catalyst

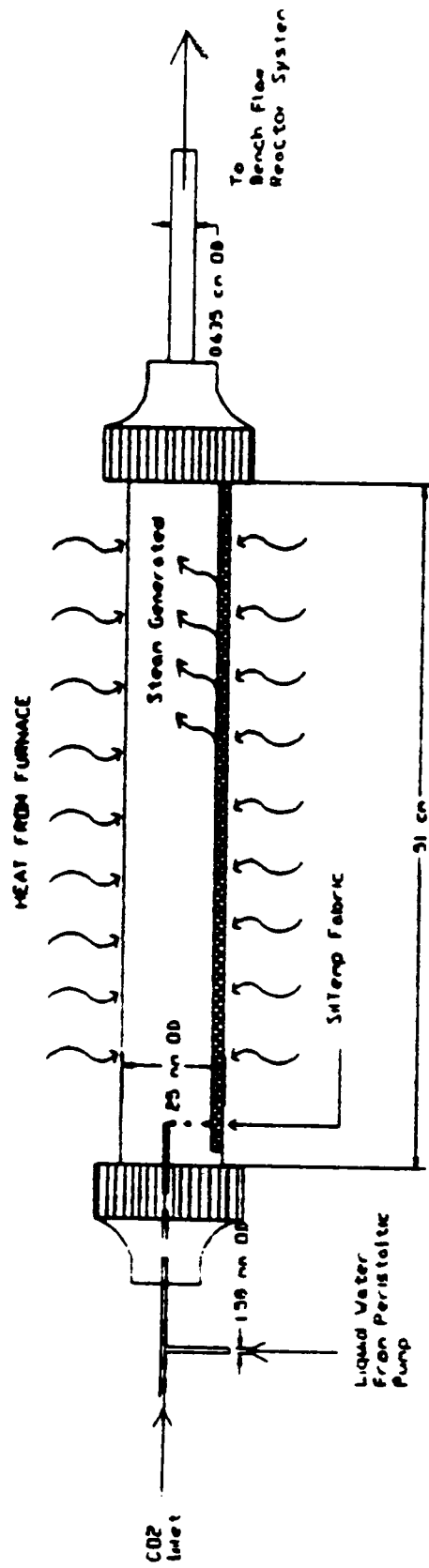


Figure 5: Steam Generator

sample, the plumbing downstream of the steam generator is heated using a Thermolyne<sup>TM</sup> heating tape in conjunction with a Digi-Sense<sup>TM</sup> temperature controller. The heating tape is wrapped around the steam lines and a fiber silica blanket is used as an insulator to minimize heat loss to the surroundings. For typical runs, the temperature controller maintains the heating coil such that the lines downstream of the steam generator are at 250° C.

### **3.3.3 Water Condenser**

In order for a dry gas analysis to be conducted on the exhaust gases by the gas analyzers, the water vapor in the gases has to be removed. The formation of the liquid droplets in the analyzers could potentially damage the analyzers and lead to inaccurate results. Therefore, a condenser is used to remove water from the exhaust gas. The hot gases from the reactor leave the furnace at approximately 100-600° C depending on the particular test being conducted. Therefore, the condenser needed to cool the water vapor below its dew point temperature in order for the water vapor present in the feed stream to condense. The condenser is built similar to a shell and tube type heat exchanger with parallel flow. The cold refrigerant fluid, which is a 60-40 mixture of glycol and water, enters the outer shell consisting of a stainless steel cylinder with a 20.32 cm diameter and 0.635 thick. The cold refrigerant is maintained at 0° C by a FTS chiller, Model RC-210.

As illustrated in Figure 6, the hot reactor gases flow into the condenser through coiled 0.635 cm stainless steel tubing. These gases then flow into a second stainless steel cylinder with a 7.62 cm inside diameter and a 0.3175 cm wall thickness. The second cylinder acts as a collection area for the condensed water that accumulates during the testing process. A drain is attached to the bottom of each cylinder to allow the condensed water to be removed after test runs are completed.

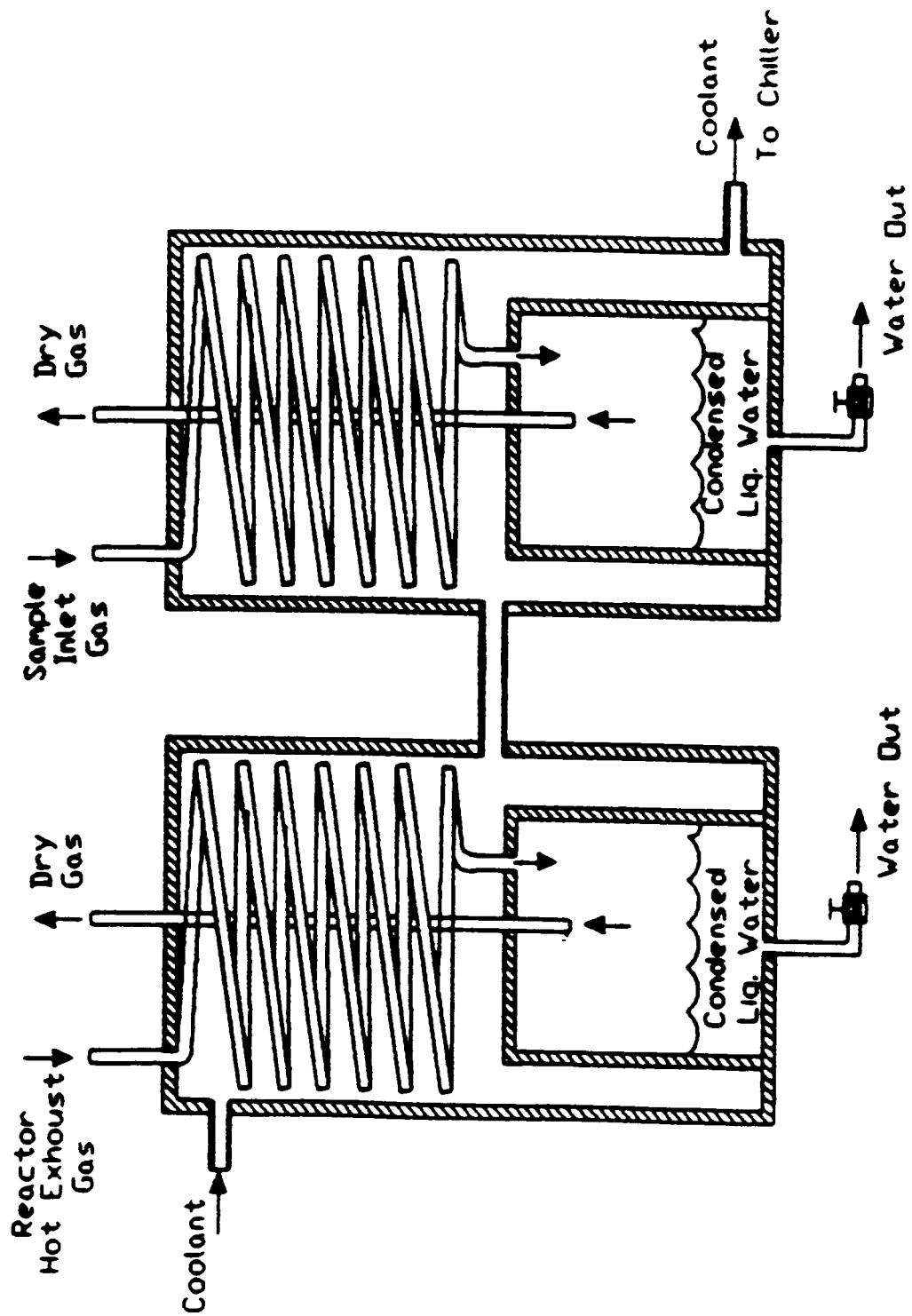


Figure 6: Water Condenser

### **3.4 Flow System**

#### **3.4.1 Mass Flow Controllers**

The feed stream gas, originally in cylinders, is blended using Tylan mass flow controllers (Model FC280). A total of 18 mass flow controllers are used for the bench-flow reactor. The Tylan mass flow controller is a self-contained, closed loop control system which measures the mass flow rate of gases flowing through the instrument, compares this with an externally commanded flow rate. The flow controller consists of a flow sensor, a bypass flow splitter, which determines the full scale range of the measuring section, a control valve and the electronics which condition the flow signal and drive the control valve. The Tylan mass flow controller requires a +/- 15 volt DC power supply. The Tylan power supply Model PS-17A supplies the necessary voltage for 7 mass flow controllers in the bench flow reactor. The flow controllers are divided into 3 sets (banks) of 4 each. They are designated as Bank A , Bank B and Bank C. Bank A and B contain the same set of gases: CO, O<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> while Bank C contains CH<sub>4</sub>, and NO<sub>x</sub>. The purpose of having Bank A and B with the same gases is to provide a cyclic variation of lean and rich pulses during cycled testing. This cyclic variation occurs in real engines and is simulated in the bench-flow reactor with Bank A being designated the rich bank (less O<sub>2</sub>) and Bank B the lean bank (more O<sub>2</sub>). The process of cycling is investigated further in the following sections. The carbon-dioxide enters the bench-flow reactor through the steam generator and is blended in a parallel route with Bank A, Bank B and Bank C gases.

#### **3.4.2 Solenoid Valves with Frequency Generator**

A typical internal combustion engine contains rich and lean pulses as the gaseous fuel is injected into the combustion chamber. A rich pulse is defined as a mixture

containing a hydrocarbon fuel bias or a larger concentration of fuel is found in the gaseous mixture than is found at a stoichiometric operating point. Similarly, a lean pulse can be defined by a lower concentration of fuel than is found at stoichiometric and can be seen to have a higher air/fuel ratio. In today's modern engines, the oscillation that occurs about the stoichiometric point can be attributed to a feedback sensor called an Exhaust Gas Oxygen valve ,or EGO sensor. This device samples the exhaust gas to determine whether the engine is operating at a lean or rich bias. After the sampling, the EGO sensor has the capability of allowing either more oxygen when a rich bias is found or less oxygen when lean conditions are determined to enter the combustion chamber. Therefore, as the sensor continually adjusts the feed stream composition, a cycling effect takes place. In order to simulate this cycling effect in the bench flow reactor, two solenoid valves in conjunction with a frequency generator are employed. As mentioned previously, a bank of exhaust gases containing a rich bias, Bank A, and a bank of gases with a lean bias, Bank B, are used. These banks are connected to the rich and lean solenoid valves and a frequency generator is used to energize these valves at a frequency between 0-2 Hz for standard test runs. Real engine cycling may be at a much higher frequency, however this high frequency can not be simulated by the current design.

### **3.4.3 Pressure Transducers**

Four pressure transducers are used to measure the pressure at various locations in the bench-flow reactor. The Omega pressure transducer, Model PX811, is used with an analog output from 0-10 volts. This analog signal is sent to Omega DP41-S high performance process indicators. The pressure transducers operate at a range of 0-20 psia and are used to measure the system, reactor, vent and analyzer pressures and are designated P1, P2, P3 and P4, respectively. During pulsing of the feed stream, Bank A and B are switched on and off. In one half of the cycle, Bank A is fed through the

reactor and in the other half cycle Bank B is fed through the reactor. It should be noted that during the pulsing mode the pressures P1 and P2 are held at a constant value so that a constant pressure gas flow is fed through the catalyst. The pressures in the bench-flow reactor are maintained constant using a Veriflo back pressure regulator valves mounted on the front panel of the bench-flow reactor.

#### **3.4.4 Temperature Sensors**

Temperature sensors are used throughout the bench-flow reactor in order to ensure that proper heating is maintained. Thermocouples inserted in the reactor above and below the catalyst are of type K. They are connected to an Omega thermocouple digital panel temperature Model DP41-TC. The temperature of the steam downstream of the steam generator is also monitored using a type K thermocouple mounted directly in the flow stream.

#### **3.4.5 Analyzers**

##### **Carbon Monoxide Analyzer**

The analyzer used for carbon monoxide detection is the non-dispersive infrared analyzer (AIA-2) built by Olson-Horiba incorporated. It is based on the principle of infrared adsorption. The specifications of the CO analyzer are shown in Table A-1 in the Appendix [24].

##### **Nitrogen Oxides Analyzer**

The analyzer used for NO/NO<sub>x</sub> is the Beckman Model 951 built by Beckman incorporated. The principle of operation is based on the chemiluminiscent method. The chemiluminiscent method for detection of NO/NO<sub>x</sub> is based on its reaction with ozone,

O<sub>3</sub>, to produce nitrogen-dioxide and oxygen. The specifications for the NO/NO<sub>x</sub> analyzer are shown in Table A-1 in the Appendix [25].

### **Hydrocarbon Analyzer**

For the purpose of detection hydrocarbons in the exhaust gas stream, a Bendix Model 8402 Total Hydrocarbon Analyzer is used. The Total Hydrocarbon Analyzer uses the technique of flame ionization detector, FID, to acquire a quantitative measurement of total hydrocarbons in a gas sample. The specifications of the hydrocarbon analyzer are shown in Table A-1 in the Appendix [26].

### **3.5 Over-View of Data Acquisition System**

The data acquisition system has been built as a part of the development of a computer-controlled laboratory bench-flow reactor capable of performing a variety of noncycled and cycled tests. These tests would complete the accurate simulation of a vehicle during warm-up and steady-state conditions.

The primary purpose of the data acquisition system, DAS, for the bench-flow reactor is to control and monitor the flow rates of the gases, temperatures, and pressures at various locations. The DAS also accomplishes the enormous task of logging real time data from the HC, NO<sub>x</sub> and CO analyzers. The DAS is capable of acquiring voltage and current signals from transducers at extremely fast rates thereby permitting accurate transient analysis. During testing, the simultaneous variation of the feed stream composition along with temperature measurements makes manual data logging virtually impossible.

The main components of DAS include the personal computer, data acquisition boards and LabView software. The data acquisition boards are a link between the user

and the bench-flow reactor and are mounted inside the personal computer, PC. They are used to control and acquire signals generated by the transducers. The mass flow controllers which are used to simulate exhaust gas are actuated by a voltage signal from 0-5 Volts by the data acquisition boards. This voltage path allows the accurate control of the valve opening thereby regulating the flow rate and hence the concentration of the exhaust gases. The temperature and pressure transducers send voltage signals which are recorded at speeds desired by the user.

The function of LabView in the DAS is to provide a user feed back and control loop for the components in the system. A LabView program is used to facilitate the user to run the bench-flow reactor and acquire data simultaneously. LabView interacts with the data acquisition boards which in turn control and monitor the operation of the bench-flow reactor.

The DAS includes controlling the reactor furnace in order to simulate variable time dependent temperature profiles and control of the peristaltic pump. Figure 7 provides an over-all illustration for the interface between the computer and the bench-flow reactor system. The boards (AT-AO-6/10 and AT-MIO-64F5) shown are actually mounted inside the computer, and are shown outside the computer for illustration purposes. The boards are connected to the connector blocks mounted on the design board. These connector blocks are then linked to the data acquisition boards via cables. Figure 7 also shows the channels used for specific mass flow controllers, temperature sensors, pressure sensors and the CO and NO<sub>x</sub> gas analyzers.

It should be noted that the hydrocarbon analyzer was used independently of the DAS system and the hydrocarbon data was read directly from the analyzer.

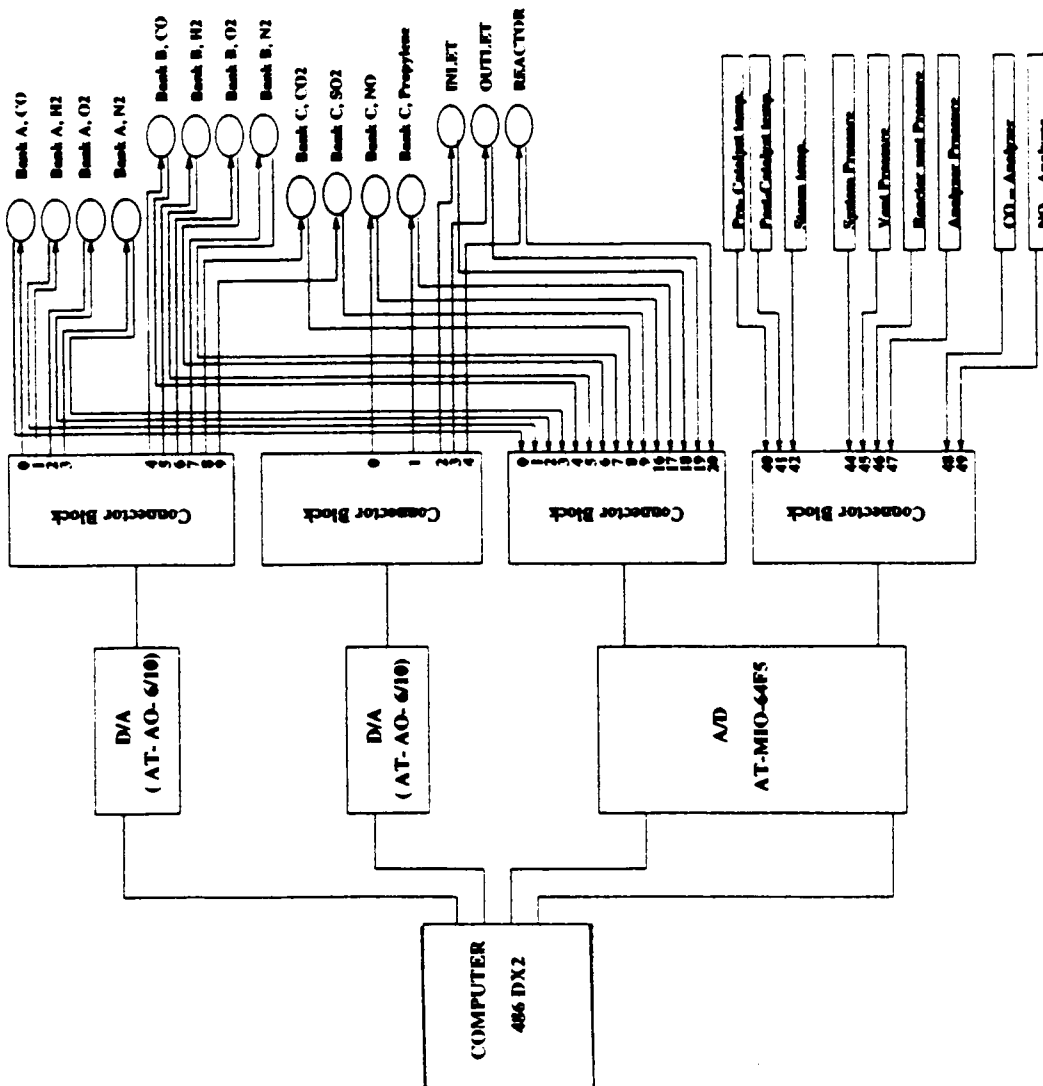


Figure 7: Schematic Diagram of Interface between PC and Bench-Flow Reactor

### **3.5.1 Components of the Data Acquisition System**

#### **Computer**

The PC used for the control of the bench-flow reactor is an IBM, 486DX, 66Mhz computer. The PC is also equipped with 3 data acquisition boards. These boards are mounted inside the PC and include 2 digital to analog boards(AT-AO-6/10) and 1 analog to digital board(AT-MIO-64F5).

#### **Data Acquisition Boards**

There are a total of 3 data acquisition boards incorporated into the bench-flow reactor system, 2 of which are used for control and 1 is used for data acquisition. The data acquisition boards are manufactured by National Instruments Inc. and are classified as digital to analog (D-A) or analog to digital (A-D). The control boards (D-A) are used for sending voltages from the computer to the bench-flow reactor. The data acquisition board (A-D) is used for acquiring signals such as temperature, pressure and analyzer output from the bench-flow reactor. Each (D-A) board has 10 channels, whereas the (A-D) board has 32 differential channels and 64 single-ended channels.

#### **LabView**

LabView is a graphical software developed by National Instruments for the purpose of controlling and acquiring data from a variety of processes. LabView is capable of performing complex mathematical functions on the data and providing the output of this analysis in a user-prescribed format. For example, instead of writing a FORTRAN program to add two numbers, LabView uses a symbolic notation thereby making it simple and easy to use. In essence, LabView revolves around developing a

"vi", called a visual instrument, which is used to describe the system and thereby controlling user-defined parameters such as volumetric flow rates and temperatures.

### **Control Board**

The control board is a link between the data acquisition boards and the actual instruments. Since there are 18 mass flow controllers, 3 temperature sensors, 4 pressure sensors and 5 analyzers, accurate bookkeeping of the various channels becomes difficult and therefore a control board is needed. The control board has the advantage of being easily accessed and debugged. The 18 mass flow controllers are divided into 4 banks, where Bank A and Bank B consist of 4 mass flow controllers each and are used for switching purposes; i.e., to simulate the cyclic behavior of the exhaust gas stream. Bank A and Bank B consist of gases CO, O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>. In addition, Bank C also contains 4 channels corresponding to the CH<sub>4</sub>, SO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub> mass flow controllers. Finally, there is a calibration bank which contains mixtures of CO, CH<sub>4</sub>, and NO<sub>x</sub>. These gases are used to ensure the accuracy of the analyzers during testing.

### **Design of the Control Board**

Figure A-1 in the Appendix shows a schematic of the top view of the control board. The control board has 4 connector blocks mounted on its top side. Two connector blocks are used for the A/D board and 2 for the D/A board. To make debugging easy, the following color code is used for the mass flow controllers in the various banks.

Red tape on the cable indicates [Bank A]

Black tape on the cable indicates [Bank B]

Blue tape on the cable indicates [Bank C]

Yellow tape on the cable indicates [Calibration Bank]

A combination of colors is used for the inlet, outlet and reactor mass flow controllers.

Each power supply (PS-17A) can supply up to 7 mass flow controllers and there are a total of 3 power supplies incorporated into the system. Details of the channel assignments for the power supplies are shown in Table A-1 in the Appendix.

- 1) The first power supply supplies power to mass flow controllers in Bank A and 3 channels of Bank B.
- 2) The second power supply supplies power to 1 channel of Bank B, 4 channels of Bank C and 2 calibration bank channels.
- 3) The third power supply provides power to 1 channel of the calibration bank and 3 total flow channels (inlet, reactor and outlet).

Figure A-2 in the Appendix provides a detailed sketch showing the connections for a typical mass flow controller. The mass flow controller is connected to the terminal blocks which in turn are connected to the power supplies and subsequently to the connector blocks. The power supplies used to drive the mass flow controllers are labeled PS1, PS2, and PS3. The terminal blocks are used to minimize the number of wires running from the 18 mass flow controllers to the connector blocks.

### **DAS Operation**

The DAS is an open loop control system in which the bench-flow reactor is controlled by voltage signals sent from the PC. As mentioned earlier, the main component controlled by the DAS is the Tylan mass flow controllers.

Once the required flow rates and temperatures are decided upon for a particular run, the LabView program can be initiated and the flow rates for the various gases in cc/min can be keyed in. After selecting the start key on the LabView console, the system is ready to run. The LabView program is used to convert the desired flow rates to

voltages based on the conversion factors for the particular mass flow controllers. These voltages would then be sent to the mass flow controllers via the digital to analog board (AT-AO-6/10). The valves of the mass flow controllers would then close or open based on the amount of voltage needed to match the desired flow rate.

The chosen flow rate remains the same on the particular mass flow controller unless it is changed and LabView is reinitialized. It is advisable to change all the flow rates to 0.0 before turning off the system, this would prevent the gas flowing during system start-up, since the D/A boards would hold the voltage as long as the power is on.

The DAS also has a data logging capability. The data from the temperature, pressure and analyzers are recorded in real time. The thermocouples record the temperatures and pass the voltage to the A/D board, which is then read by the specific "vi" program written in LabView. Pressure signals and signals for the various analyzers are also recorded. The sequence shown below is the operations to be performed before running the bench-flow reactor.

- 1) Turn on the computer.
- 2) Start LabView (this is done by clicking on the LabView window).
- 3) Double click on the subdirectory BENCHFLO.
- 4) Open BFR-CTR file.
- 5) Set the flow rates for the various gases in cc/min.
- 6) Check whether the gas bottles are opened and the toggle switches on the mass flow controllers are in the open position.
- 7) Run the system.

### **3.6 Operation of the Bench-Flow Reactor**

#### **3.6.1 Start-up Procedure**

The step-by-step start-up procedure for the bench-flow reactor proceeds as follows. First, the main electrical switches located on the power strips on the back of the unit are switched to the ON position. This energizes the frequency generator, the power supplies, the temperature controller, both reactors, the solenoid valves, as well as the Omega pressure and temperature sensors located on the front panel. Once the system has been activated, approximately 15 minutes are required for the heating tape on the steam lines and the Lindberg furnaces to reach preset temperatures. While the system is heating up, all of the mass flow controllers' toggle switches are in the off position (down). The toggle valves should be in the off position when the bench-flow reactor is not in operation. With all the toggle switches down, the gas bottles used to simulate the exhaust gas can be opened and the outlet pressure of the pressure regulators is set at 20 psig. Once the system has reached the desired temperatures, it is important to begin the steam generation cycle prior to introducing the inlet gases into the system. In doing so, the pressure built-up from the steam would prevent the flow of the simulated exhaust gases into the plumbing of the steam generator via the three-way connector at the inlet of the reactor. To begin the steam generation process, the level of the water in the reservoir needs to be checked. This reservoir should be filled with distilled water so that contaminants and impurities do not enter the laboratory reactor system. When the distilled water enters the steam generator, make sure that the Siltemp<sup>TM</sup> fabric, which acts as the "wick" of the system, is placed in the center of the quartz tube. Once the water has entered the steam generator, and steam is being produced, the mass flow controllers can be energized from the LabView, BFLOW.CTRL program. The CO<sub>2</sub> mass flow controller toggle switch can now be turned on. Approximately 15 minutes are required for the pressure to build up in the lines downstream of the steam generator

before testing can begin. Once steady state conditions are reached for the system, the inlet gases are then introduced into the bench flow reactor by flipping the toggle valve switches up.

### 3.6.2 Test Modes

The bench-flow reactor can operate in three different sampling modes by the 3-way valves and the 4-way valve located on the front control panel. One such mode of testing concerns the conversion efficiency of the catalyst being examined. To do this testing it is necessary to analyze the simulated inlet exhaust gas stream prior to catalysis. In order to acquire the inlet gas concentrations, the 3-way valves and 4-way valve should be placed in the precatalyst sampling position as shown in Figure 8.

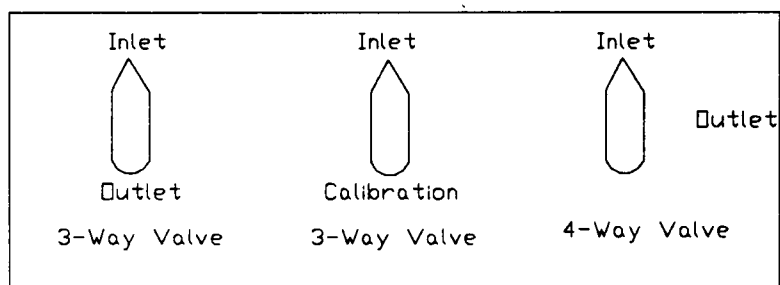


Figure 8: Bench-Flow Reactor Precatalyst Sampling

To analyze the exhaust gas after catalysis, or post catalysis, the 3-way and 4-way valves on the control panel are placed in the positions depicted in Figure 9.

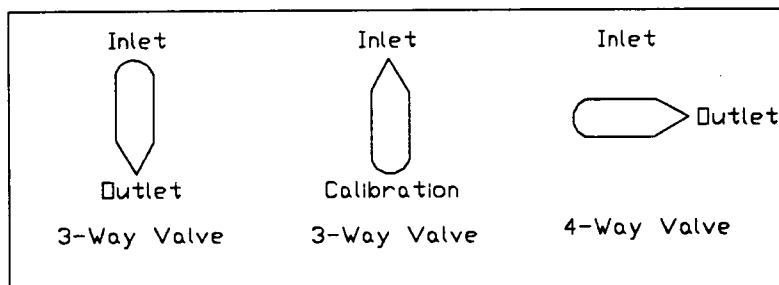


Figure 9: Bench-Flow Reactor Post-catalyst Sampling

The third mode of operation for the bench-flow reactor is the calibration mode. This mode is used to ensure the ongoing accuracy of the analyzers by testing the analyzers' output in percent concentrations versus the known gases' concentration from the calibration bank, Bank C. This mode of operation is achieved by placing the 3-way and 4-way valves as shown in Figure 10.

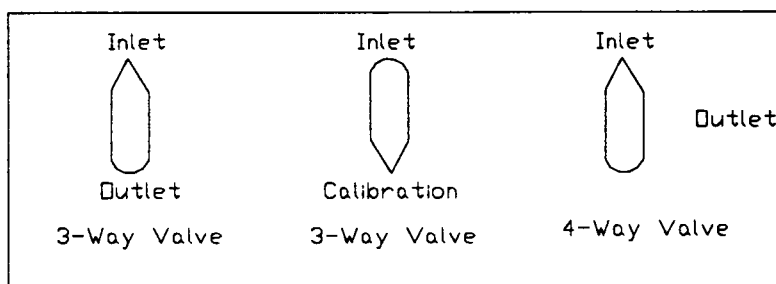


Figure 10: Bench-Flow Reactor Calibration Gas Sampling

### 3.7 Experimental Testing

#### 3.7.1 Light-off Tests

In order to evaluate the catalysts performance under different types of conditions, several types of experimental testing are carried out. Light-off test are chosen since they

are commonly used to evaluate catalyst behavior and performance on engine dynamometers. Light-off tests demonstrate the effect of temperature on the conversion efficiencies of the constituents and are typically used to find the light-off temperature of the catalyst. The light-off temperature is defined as the temperature at which 50% conversion of the constituent is reached. The light-off tests for these experiments are used in three different approaches: lean and rich noncycled light-off tests and stoichiometric cycled light-off tests.

A decreasing temperature program was used from 570° C to 100° C for the light-off tests. The reason for the decreasing temperature program was due primarily to the heat transfer capabilities of the system. Published light-off testing suggested a decreasing temperature program at 7° C/min should be used to ensure that steady-state catalyst temperatures are reached and for the repeatability of the experiments[27]. This incremental temperature change was not possible or controllable as the reactor temperature increased due to the observed rate of the furnace temperature increases of 60° C/min. Therefore, better temperature control and steady-state conditions were established as a result of cooling the catalyst sample from elevated temperatures at an acceptable rate by the use of an insulated jacket placed around the reactor test section. With the insulation in place, the average cooling rate of the catalyst sample was 8.3° C/min during the testing process.

### **3.7.2 Cycled Stoichiometric Light-off Tests**

The stoichiometric cycled light-off tests involve cycling the feed gas between two banks of exhaust gases by the use of solenoid valves driven by a frequency generator. The first bank, Bank A, is used to simulate the rich environment and contains a low oxygen concentration when compared to stoichiometric. The second bank, Bank B, is

used to simulate a lean environment and contains a larger amount of oxygen on a volumetric basis than stoichiometric. Bank A and Bank B are identical in their constituent composition with the exception of the oxygen constituent reflecting the lean or rich bias. The nitrogen volumetric flow rate also changes to permit the same flow rate of gas entering the feed stream from both banks.

To accurately simulate an NGV vehicle, it is important to scale down the volumetric flow rate and catalyst volume occurring in a "real" engine exhaust configuration to the simulated conditions on the bench-flow reactor. It would be impractical and costly to design a model reactor to the same size and configuration as the exhaust arrangement in automobiles; therefore, a critical step in evaluating natural gas catalyst is to simulate the exhaust constituents as closely as possible.

Based on published model reactor studies for NGV simulations, the necessary constituents for an accurate portrayal of NGV exhaust in cycled stoichiometric operation is shown in Table II [28].

Table II: Cycled Stoichiometric NGV Simulation

| Constituent      | By Volume   | Volumetric<br>Flow Rate | Bottle Conc.<br>of Constituent | Bottle Flow<br>Rate |                       |
|------------------|-------------|-------------------------|--------------------------------|---------------------|-----------------------|
|                  |             | (cc/min)                |                                | (cc/min)            |                       |
| CO               | 1%          | 48.42                   | 20%                            | 242.1               |                       |
| H <sub>2</sub>   | 33 ppm      | 16                      | 40%                            | 40                  |                       |
| O <sub>2</sub>   | 0.59-1.88%  | 28.5-91                 | 100%                           | 28.5-91             |                       |
| CH <sub>4</sub>  | 1500 ppm    | 7.3                     | 100%                           | 7.3                 |                       |
| NO               | 1000 ppm    | 4.8                     | 1.02%                          | 470.6               |                       |
| CO <sub>2</sub>  | 14%         | 677.9                   | 100%                           | 677.9               | Sat. H <sub>2</sub> O |
| H <sub>2</sub> O | 10%         | 484.2                   |                                | 484.2               | 0.4 cc/min            |
| N <sub>2</sub>   | Carrier gas | 3582-3535               | 100%                           | 2891-2828           |                       |

The total volumetric flow rate across the catalyst of was 4.842 standard liters per minute, SLPM. The catalyst volume used in the testing was 5.6 cm<sup>3</sup> which resulted in a

space velocity of  $52,000 \text{ hr}^{-1}$ . A cycling frequency of 0.5 Hz is used to drive the solenoid valves to provide the realistic oscillation typically occurring for engines operated at stoichiometric.

In order to verify the published stoichiometric simulation, the redox ratio is used. The redox ratio,  $R$ , is the ratio of the reducing to the oxidizing components in the feed gas and is related to the air/fuel ratio. The redox ratio can be found by the following relation:

$$R = \frac{[\text{CO}] + [\text{H}_2] + 4[\text{CH}_4]}{[\text{NO}] + 2[\text{O}_2]} \quad (1)$$

where the constituents are in a volumetric percentage basis [13].

A redox ratio equal to one represents a stoichiometric feed stream since the reducing and oxidizing components are in equilibrium. A redox ratio less than one indicates the mixture is fuel-lean since the oxidizing components represent the larger percentage of the constituents. Similarly, the redox ratios greater than one indicate a fuel rich feed stream.

As can be seen from Table II for the cycled stoichiometric simulation, the rich, or net-reducing, Bank A contains 0.59% oxygen in the feed stream. By the relation described in equation (1), this corresponds to a redox ratio of 0.5 ( $R=0.5$ ). In the lean, or net-oxidizing, Bank B, the feed stream contains 1.88% oxygen in the feed stream resulting in a redox ratio of 1.5. Therefore during the cycling action between the lean and rich feed streams at 0.5 Hz, a redox ratio of 1 is obtained, which indicates a cycled stoichiometric feed stream. As a result, a realistic NGV exhaust simulation is achieved.

### 3.7.3 Noncycled Lean Light-off Tests

The NGV simulation based on a noncycled lean light-off test is shown in Table III [28]. The total volumetric flow rate and the space velocity used in the noncycled lean simulation are similar to the stoichiometric feed stream. The redox ratio for this test is 0.545 which is less than one and therefore represents a fuel-lean bias.

Table III: Noncycled Lean NGV Simulation

| Constituent | By Volume   | Volumetric<br>Flow Rate<br>(cc/min) | Bottle Conc.<br>of Constituent | Bottle Flow<br>Rate<br>(cc/min) |            |
|-------------|-------------|-------------------------------------|--------------------------------|---------------------------------|------------|
| CO          | 1%          | 48.42                               | 20%                            | 242.1                           |            |
| H2          | 0.33%       | 16                                  | 40%                            | 40                              |            |
| O2          | 1.72%       | 83.3                                | 100%                           | 83.3                            |            |
| CH4         | 1500 ppm    | 7.3                                 | 100%                           | 7.3                             |            |
| NO          | 1000 ppm    | 4.8                                 | 1.02%                          | 470.6                           |            |
| CO2         | 14%         | 677.9                               | 100%                           | 677.9                           | Sat. H2O   |
| H2O         | 10%         | 484.2                               |                                | 484.2                           | 0.4 cc/min |
| N2          | Carrier gas | 2836.6                              | 100%                           | 2836.6                          |            |

### 3.7.4 Noncycled Rich Light-off Tests

For the noncycled rich NGV simulation, the feed stream has to reflect a net-reducing environment. This was accomplished by reducing the percentage of oxygen from 1.72% for the lean case to 0.5% for the rich bias. This resulted in a redox ratio of 1.755 which is greater than 1 and therefore represents a fuel-rich feed gas. The noncycled rich NGV simulation is shown in Table IV [28].

Table IV: Noncycled Rich NGV Simulation

| Constituent      | By Volume   | Volumetric | Bottle Conc. | Bottle Flow |                       |
|------------------|-------------|------------|--------------|-------------|-----------------------|
|                  |             | Flow Rate  | of Const.    | Rate        |                       |
|                  |             | (cc/min)   |              | (cc/min)    |                       |
| CO               | 1%          | 48.42      | 20%          | 242.1       |                       |
| H <sub>2</sub>   | 0.33%       | 16         | 40%          | 40          |                       |
| O <sub>2</sub>   | 0.50%       | 24.2       | 100%         | 24.2        |                       |
| CH <sub>4</sub>  | 1500 ppm    | 7.3        | 100%         | 7.3         |                       |
| NO               | 1000 ppm    | 4.8        | 1.02%        | 470.6       |                       |
| CO <sub>2</sub>  | 14%         | 677.9      | 100%         | 677.9       | Sat. H <sub>2</sub> O |
| H <sub>2</sub> O | 10%         | 484.2      |              | 484.2       | 0.4 cc/min            |
| N <sub>2</sub>   | Carrier gas | 2836.6     | 100%         | 2895.7      |                       |

### 3.8 Catalyst Aging Process

In order for the catalysts to be evaluated based on continued use in commercial applications, the catalyst were aged to promote thermal degradation and reduction of the catalysts' conversion capabilities. The catalysts were aged by flowing a 0.8 L/min feed stream which alternated between Bank A containing 5% H<sub>2</sub>/N<sub>2</sub> and Bank B with 5% H<sub>2</sub>/N<sub>2</sub>. The aging process duration was 4 hours at a catalyst temperature of 1000° C. The cycling frequency used in the aging was 0.1Hz [26].

The aging process is shown in Table V with the corresponding volumetric flow rates of the hydrogen, oxygen and nitrogen.

Table V: Catalyst Aging Process

| Constituent    | By Volume   | Volumetric<br>Flow Rate<br>(cc/min) | Bottle Conc.<br>of Constituent | Bottle Flow<br>Rate<br>(cc/min) |
|----------------|-------------|-------------------------------------|--------------------------------|---------------------------------|
| Bank A         |             |                                     |                                |                                 |
| H <sub>2</sub> | 0.50%       | 40                                  | 40%                            | 100                             |
| N <sub>2</sub> | Carrier gas | 2836.6                              | 100%                           | 700                             |
| Bank B         |             |                                     |                                |                                 |
| O <sub>2</sub> | 0.50%       | 40                                  | 100%                           | 40                              |
| N <sub>2</sub> | Carrier gas | 2836.6                              | 100%                           | 760                             |

This aging process differs from the published aging program where the total volumetric is 1.0 L/min as opposed to the 0.8 L/min used for this aging process. The 0.8 L/min chosen for this process is based on the volumetric flow rate limitations of the hydrogen mass flow controller, where the maximum flow rate is 100 cc/min. Based on the desired volumetric flow rate of 1 SLPM and a bottle concentration 40% H<sub>2</sub> and 60% N<sub>2</sub>, a flow rate of 125 cc/min of hydrogen would need to be maintained, which is obviously outside the limits of the mass flow controller used. Therefore, by utilizing the maximum flow rate achievable by the mass flow controller, a total volumetric flow rate of 0.8 SLPM could be found. Although this flow rate is different than the published aging process, it is believed that the volumetric flow rate will not result in significant differences and will provide the desired aging effect especially at such a high aging temperature.

## CHAPTER 4

### RESULTS AND DISCUSSION

This chapter discusses the performance of the natural gas catalysts in regards to Pd/Rh loadings and washcoat compositions. Section 4.1 presents the performance of the natural gas catalysts under rich, lean and stoichiometric conditions. Section 4.2 investigates the effects of precious metal loading on the conversion efficiencies and light-off temperatures of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO. The effects of the washcoat composition on the over-all performance of the catalysts is presented in Section 4.3. Section 4.4 presents a detailed discussion of methane's complete oxidation process in natural gas catalysis and Section 4.5 discusses the effects of the water-gas shift reaction and the steam reforming reaction on carbon monoxide and methane conversion efficiencies. Section 4.6 investigates the aging effects on catalyst performance and durability as a result of precious metal loadings and washcoat compositions. Finally, Section 4.7 presents a detailed discussion on the thermal deactivation of the catalysts due to sintering effects and the undesirable thermal interactions that occur between the precious metals and the washcoat during high temperature aging. The conversion efficiency curves for all the catalysts tested are presented in the Appendix.

#### **4.1 Effects of Lean, Rich and Stoichiometric Feed Stream Composition on Conversion Efficiencies and Light-off Temperatures for $\text{CH}_4$ , $\text{NO}_x$ and CO**

##### **4.1.1 $\text{CH}_4$ Conversion**

Experimental results indicate that methane conversion is maximized in the following order of feed stream simulations: stoichiometric cycling > rich noncycled > lean noncycled. Figure 11 illustrates the  $\text{CH}_4$  conversion efficiencies for a fresh catalyst with

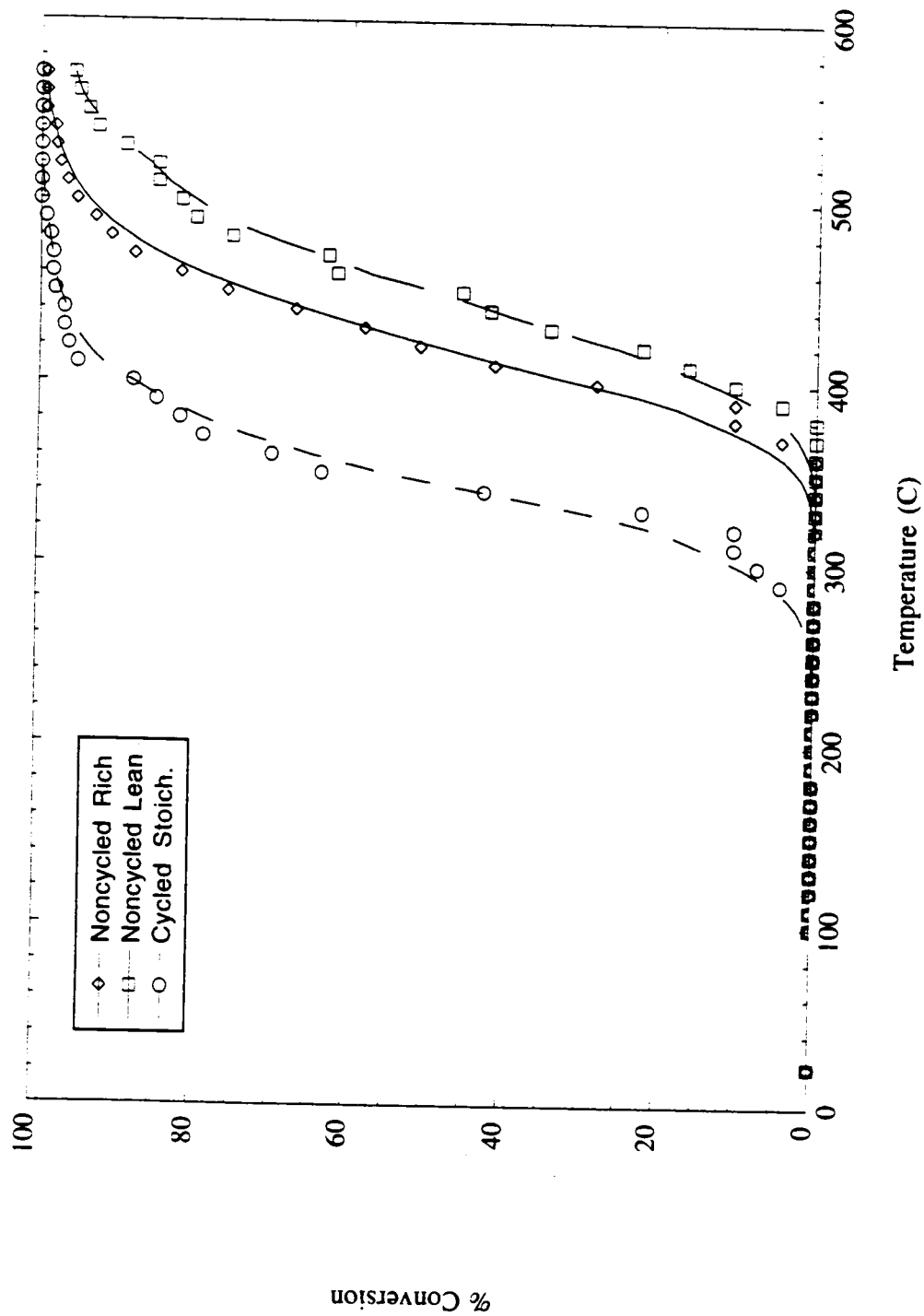


Figure 11:  $\text{CH}_4$  Conversion Efficiencies for a Fresh Catalyst with a  $60 \text{ g/ft}^3$  Pd/Rh loading and a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in Rich, Lean and Stoichiometric Lightoff Tests

a Pd/Rh loading of 60 g/ft<sup>3</sup> and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in rich, lean and stoichiometric environments. As shown in the figure, the CH<sub>4</sub> light-off temperature for the catalyst is 450° C during a noncycled lean simulation. As mentioned previously, the light-off temperature refers the temperature required for 50% conversion of the constituent. In the noncycled rich feed stream simulation where the presence of oxygen is diminished, the light-off temperature of methane is reduced to 417° C. This lower light-off temperature results in a 7% decrease in temperature as a result of the rich conditions of the feed stream. A light-off temperature of 350° C is obtained during a cycled stoichiometric simulation for the same catalyst. This light-off temperature for the cycled stoichiometric feed stream represents a 22% decrease in the light-off temperature found for the same catalyst under lean conditions and a 18% decrease in the light-off temperature during the rich feed stream simulation.

The observed decrease in the light-off temperature for methane can be explained from the difference in the adsorption strength of CH<sub>4</sub> and O<sub>2</sub>. Kinetic studies conducted over noble metal catalyst in the presence of excess oxygen, or lean environments, show that the observed rate law is first-order in methane and zero-order in oxygen [1]. Therefore in lean conditions, oxygen molecules coat the surface of the catalyst and tend to occupy the majority of the active sites available. In addition, the adsorption strength of oxygen molecules is greater than the adsorption strength of methane molecules. Thus, methane molecules have to compete with oxygen molecules for available active sites on the catalyst which in turn leads to lower conversion rates and hence a higher light-off temperature for methane in the lean feed stream simulation.

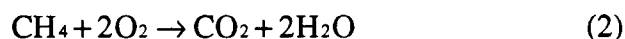
In the rich conditions, the presence of oxygen is diminished and methane molecules can compete successfully with oxygen molecules for active sites despite their weaker adsorption strength. Therefore, better conversion efficiencies and lower light-off temperatures are possible in the rich simulation as compared with the lean feed stream.

The better conversion efficiencies found for rich versus lean feed stream have also been reported by Usmen et al. [11]. For their experimental investigation, reaction studies were conducted with CH<sub>4</sub>-NO-O<sub>2</sub> mixtures in lean and rich feed streams. They found that when the feed gas had a rich bias the reduction of NO with CH<sub>4</sub> occurred by the reaction described in equation (1).



Therefore, CH<sub>4</sub> removal in the rich feed stream occurs not only by its oxidation with O<sub>2</sub>, but also by the reduction of NO by CH<sub>4</sub>. Similar results have also been substantiated by Subramanian, Kudia and Chattha [13] for the removal of methane under net-oxidizing or net-reducing conditions.

There is however a lower boundary limit for reducing the presence of oxygen in the feed stream in order to ensure a proper amount methane catalysis. As richer conditions are simulated, insufficient amounts of oxygen are adsorbed on the surface and the oxidation reaction of methane described by equation (2)



is diminished.

Recently it has been suggested that the conversion of methane conversions is maximized at a level slightly richer than stoichiometric. To explore this possibility, Oh, Mitchell and Siewert [1] conducted experiments in which the only constituents in the feed stream were CH<sub>4</sub>, CO and variable levels of oxygen. As the level of oxygen was increased from a rich, net-reducing, environment to a lean, net-oxidizing environment, CH<sub>4</sub> conversion went through a maximum at an O<sub>2</sub> concentration somewhat less than stoichiometric and then declined sharply as the O<sub>2</sub> concentration was increased further. In addition, it was found that although CO does not directly react with CH<sub>4</sub> on either side of stoichiometric, the CO constituents consumed oxygen in the feed stream and consequently reduced the CH<sub>4</sub> oxidation process.

The results of this experimental research are due to the inability of  $\text{CH}_4$  to compete effectively with CO for reactions with  $\text{O}_2$ . Consequently, better conversion efficiencies are found for the cycled stoichiometric feed stream as opposed to the noncycled rich feed stream. The increased presence of CO becomes an inhibitor for the oxidation reaction of methane during the rich feed stream simulation. As will be explained later, CO is more abundant in the rich feed stream due to the limited availability of oxygen for adequate CO oxidation.

#### 4.1.2 $\text{NO}_x$ Conversion

From the experimental results generated, the  $\text{NO}_x$  conversion efficiencies decrease on the order: noncycled rich > cycled stoichiometric > noncycled lean feed stream. Figure 12 illustrates the  $\text{NO}_x$  conversion efficiencies for a fresh catalyst with a Pd/Rh loading of  $60 \text{ g/ft}^3$  and an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in rich, lean and stoichiometric environments. As can be seen from the figure, the maximum conversion efficiency for nitrogen oxides is approximately 45% at a temperature of  $205^\circ \text{C}$  for the noncycled lean case. For the cycled stoichiometric feed stream simulation, a much better conversion efficiency is obtained and yields a light-off temperature of  $160^\circ \text{C}$ . For the noncycled rich feed stream, the  $\text{NO}_x$  conversion is much better than either the noncycled lean or the cycled stoichiometric feed stream simulation. A light-off temperature of  $140^\circ \text{C}$  is obtained for the noncycled rich feed stream. This results in a 12.5% reduction in light-off temperature for  $\text{NO}_x$  in the rich noncycled feed stream compared to the cycled stoichiometric feed stream.

The reason for the low conversion efficiency for the noncycled lean feed stream can be explained by the reduction mechanism of nitrogen oxide by carbon monoxide in the following reactions:

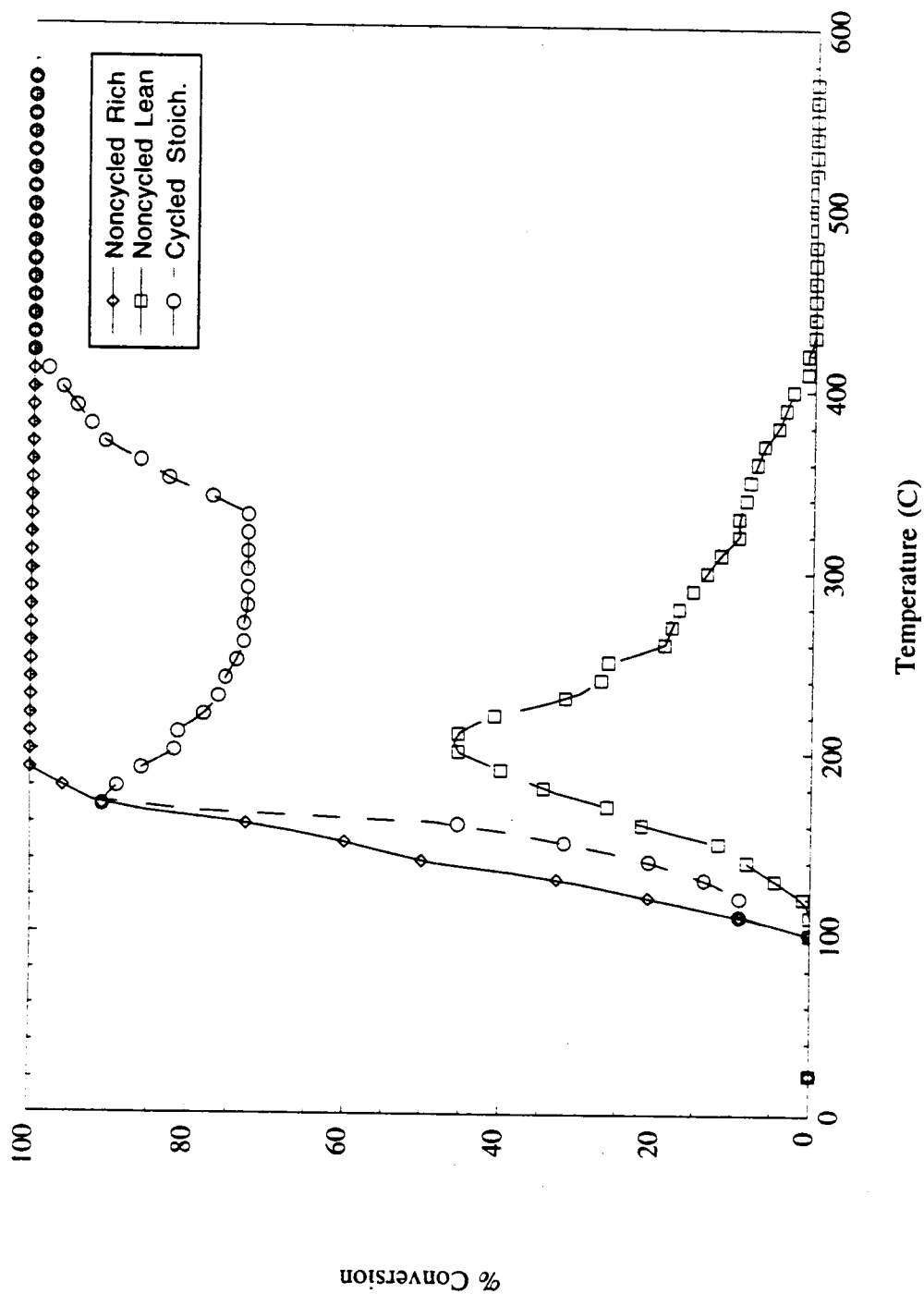
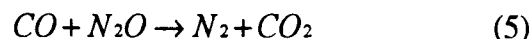
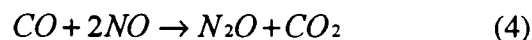
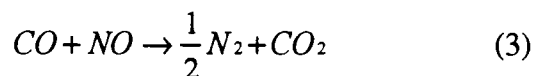
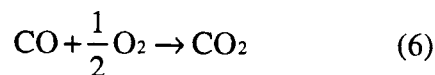


Figure 12: NO<sub>x</sub> Conversion Efficiencies for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and a Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in Rich, Lean and Stoichiometric Lightoff Tests



In the above kinetic scheme, the formation of nitrous oxide (N<sub>2</sub>O) in equation 4 is the intermediate step in the reduction reaction of NO. This formation has only been recently established as a viable reaction by researchers such as Cho, Shanks and Bailey [19] in addition to the research conducted by Hardee and Hightower [29]. The rate of the CO + N<sub>2</sub>O reaction as an intermediate step has also been shown to be as fast or faster than the rate of the overall CO + N<sub>2</sub>O reaction as concluded by Cho [30]. Therefore, the CO + N<sub>2</sub>O reaction can be said to be a very important intermediate step in the over-all reduction of NO. However, the reaction described by equation (3) represents a direct pathway for N<sub>2</sub> formation which is favored at elevated temperatures over the intermediate CO + N<sub>2</sub>O reaction [21].

During the noncycled lean feed stream, the initial increase in conversion efficiency as the catalyst temperature increases and the subsequent reduction in conversion as the catalyst temperature continues to increase can be explained by the above kinetic scheme. From the reactions described in equations 3, 4 and 5, the CO-NO reaction is of primary importance for the reduction of NO in the feed stream. The reduction of nitrogen oxide by carbon monoxide can occur only when carbon monoxide is present in the feed stream. As will be discussed later, the carbon monoxide oxidation reaction is



and during lean feed stream simulations this oxidation reaction occurs very rapidly.

As the temperature of the catalyst increases in the lean feed stream, less CO is available for reducing NO. Therefore, the NO conversion efficiency reaches a maximum

while CO is still present in the feed stream and subsequently decreases as CO is completely converted with increasing catalyst temperature. Note that the decrease in conversion efficiency for NO is not a spike or sharp peak but a gradual downward slope. The reason for this gradual decrease in conversion efficiency is that NO is also being reduced by CH<sub>4</sub> in the feed stream by the reaction described by equation (1)



This reaction continues until the oxidation of methane reaches maximum levels. At this point, there is not enough methane to reduce the NO constituent effectively and consequently the NO conversion efficiency decreases at elevated temperatures as shown in Figure 12.

The advantage of the stoichiometric versus lean conditions is due to the cycling process during the feed stream simulation where the NO molecules can be reduced by the CO-NO and CH<sub>4</sub>-NO reactions. During this cycling process, excursions to the lean, or net-oxidizing, feed stream result in limited reactions with CO and CH<sub>4</sub> due to their limited availability as shown previously for the noncycled lean case; however, during the rich, or net-reducing, feed stream, the NO reduction reactions with CO and CH<sub>4</sub> occur and effectively reduce the NO constituent in the process.

The reaction of NO with CO and CH<sub>4</sub> also explains the characteristic dip that occurs for the cycled stoichiometric conversion curve. As will be seen in the next section, CO oxidation occurs very rapidly in stoichiometric environments. Therefore, when the CO constituent is no longer present in the feed stream, the reactions described by equations (3-5) cannot occur which subsequently reduces the NO conversion efficiency. However, at higher catalyst temperatures, the CH<sub>4</sub>-NO reduction reaction described by equation (1) becomes significant and results in the complete conversion of NO in the feed stream.

The higher NO conversion efficiency found for the noncycled rich feed stream as opposed to lean and stoichiometric environments is due to the increased presence of CO and CH<sub>4</sub> in the feed stream resulting in the reduction reactions shown in equations (1),(3),(4) and (5).

The activity rates of these reactions can be said to be heightened in the rich as opposed to the lean and stoichiometric simulations as a consequence of larger amounts of carbon monoxide and methane available for the reduction reactions to take place. Therefore, to obtain maximum conversion efficiencies and hence lower light-off temperatures of the NO constituent, the noncycled rich feed stream simulation is favored.

#### 4.1.3 CO Conversion

The conversion efficiency of CO decreases in the following order: cycled stoichiometric > noncycled lean > noncycled rich feed stream. Figure 13 illustrates the CO conversion efficiencies for a fresh catalyst with a Pd/Rh loading of 60 g/ft<sup>3</sup> and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in rich, lean and stoichiometric environments. As can be seen from the figure, the light-off temperature of CO is 205 ° C under rich conditions. For the lean noncycled feed stream, a light-off temperature of 186 ° C is observed. Similarly, a light-off temperature of 160 ° C is obtained for 50% conversion of carbon monoxide during the cycled stoichiometric feed stream. Thus, a 21.9% light-off temperature reduction is achieved by the cycled stoichiometric feed stream over the noncycled rich simulation, and a 14% advantage is found for the cycled stoichiometric over the noncycled lean feed stream.

The lower conversion of carbon monoxide under rich or net-reducing conditions can be explained quite simply by the oxidation reaction shown previously in equation (6):

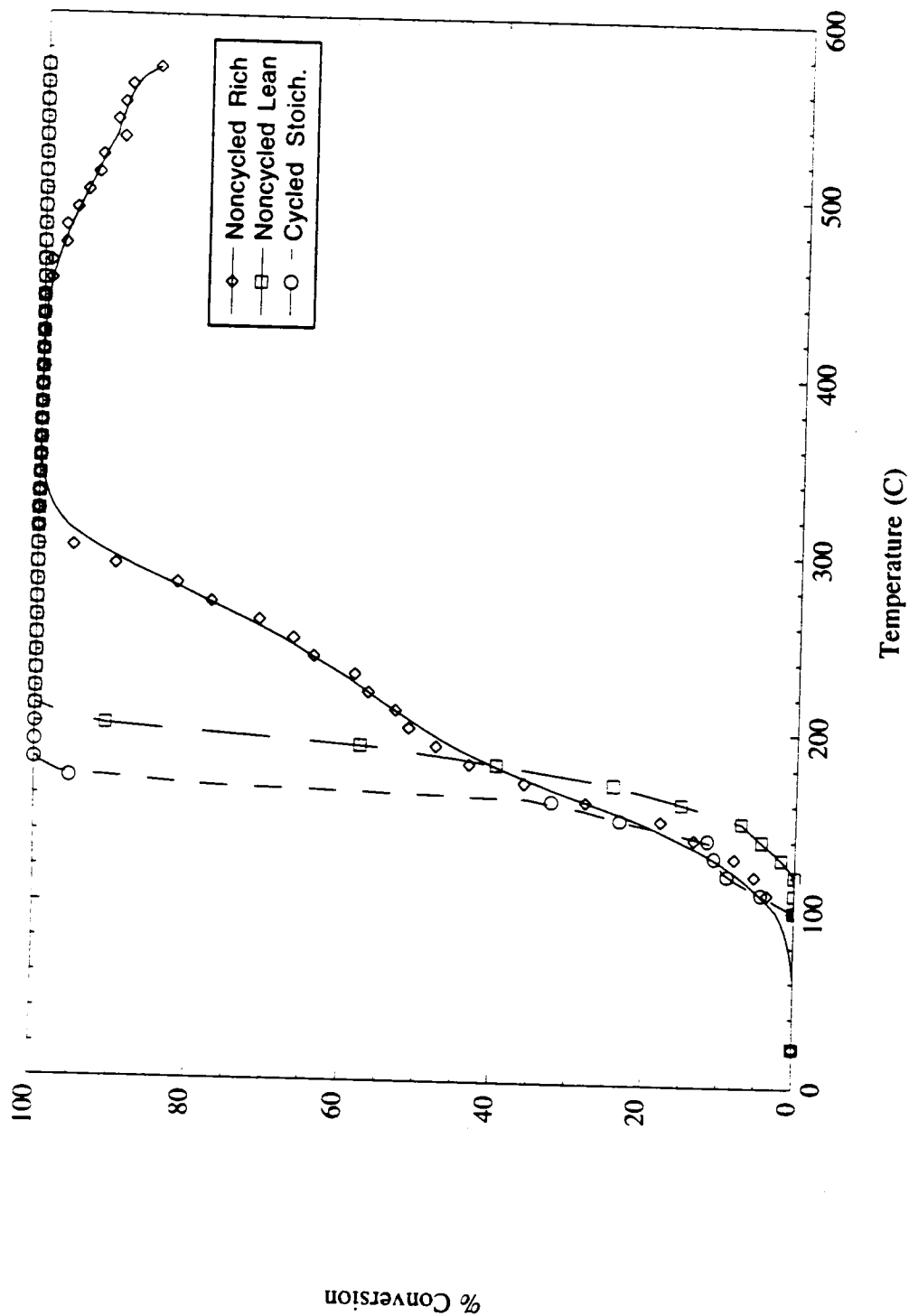
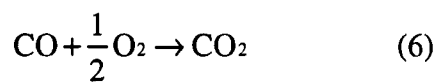


Figure 13: CO Conversion Efficiencies for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and a Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in Rich, Lean and Stoichiometric Lightoff Tests



Since there is less oxygen available under a net-reducing condition for the oxidation reaction to occur, the carbon monoxide conversion efficiency is decreased and a higher light-off temperature results.

For the comparison of cycled stoichiometric versus noncycled lean feed streams in CO conversion, theoretical reasoning must be utilized to explain the higher conversion efficiency and lower light-off temperatures encountered in the cycled stoichiometric environment. From the CO oxidation reaction shown above, it appears that higher levels of oxygen in the feed stream would result in higher conversion efficiencies than those found during a cycled stoichiometric feed stream. However, this is not the case. It is theorized that the lower CH<sub>4</sub> conversion problems encountered previously in the presence of excess oxygen can also be encountered in the oxidation conversion of carbon monoxide. As the level oxygen is increased in the feed stream, the oxygen molecules tend to occupy more activation sites needed for the adsorption and subsequent dissociation of the carbon monoxide on the catalyst surface. This in turn leads to the argument that there is indeed a optimal level of excess oxygen required for maximizing the conversion efficiency of carbon monoxide.

Another possible reason for the higher light-off temperatures found in noncycled lean simulations as opposed to the cycled stoichiometric feed stream is the increased presence of NO in the reactant stream for the lean case (See Figure 10). Oh and Carpenter [14] have found that the presence of NO prevents the occurrence of the CO-O<sub>2</sub> reaction, described in equation (6), until the CO-NO reaction becomes significant. Therefore, under lean, or net-oxidizing, environments, a higher light-off temperature could result from the prevalence of NO in the feed stream hampering the oxidation reaction of CO. In the cycled stoichiometric feed stream, less amounts of NO abound, thus a higher

rate of CO oxidation kinetics results in lower light-off temperatures and higher conversion efficiencies.

## **4.2 Effects of Precious Metal Loading on the Conversion**

### **Efficiencies and Light-off Temperatures of CH<sub>4</sub>, NO<sub>x</sub> and CO**

#### **4.2.1 Methane Oxidation**

To study the effects of loading on the conversion efficiencies and light-off temperatures, catalysts with loadings of 10, 40 and 60 g/ft<sup>3</sup> are used. The catalysts chosen for this study consist of an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat tested in a cycled stoichiometric feed stream. The cycled stoichiometric simulation is chosen for discussion in this section since it represents the closest feed stream representation of an I.C. engine. As shown in Figure 14, the light-off characteristics of the catalysts are improved as the Pd/Rh loadings are increased. A light-off temperature of 340° C is obtained at a loading of 60 g/ft<sup>3</sup>. Similarly, the light-off temperatures for the 10 and 40 g/ft<sup>3</sup> loadings are 417° C and 365° C, respectively. From these results, a light-off temperature decrease of 7.4% occurs when the Pd/Rh loading increases from 40 to 60 g/ft<sup>3</sup>. In addition, a light-off temperature decrease of 22.6% occurs when the Pd/Rh loading is increased from 10 to 60 g/ft<sup>3</sup>. As will be discussed later, the reason for the increased CH<sub>4</sub> conversion with increased Pd/Rh loadings is due primarily to the larger catalytic surface area and consequently more available active sites with higher loadings.

#### **4.2.2 Nitrogen Oxide Reduction**

The effect of loading on the light-off behavior of NO<sub>x</sub> in a cycled stoichiometric feed stream is shown in Figure 15. For a 50% conversion efficiency of nitrogen oxides,

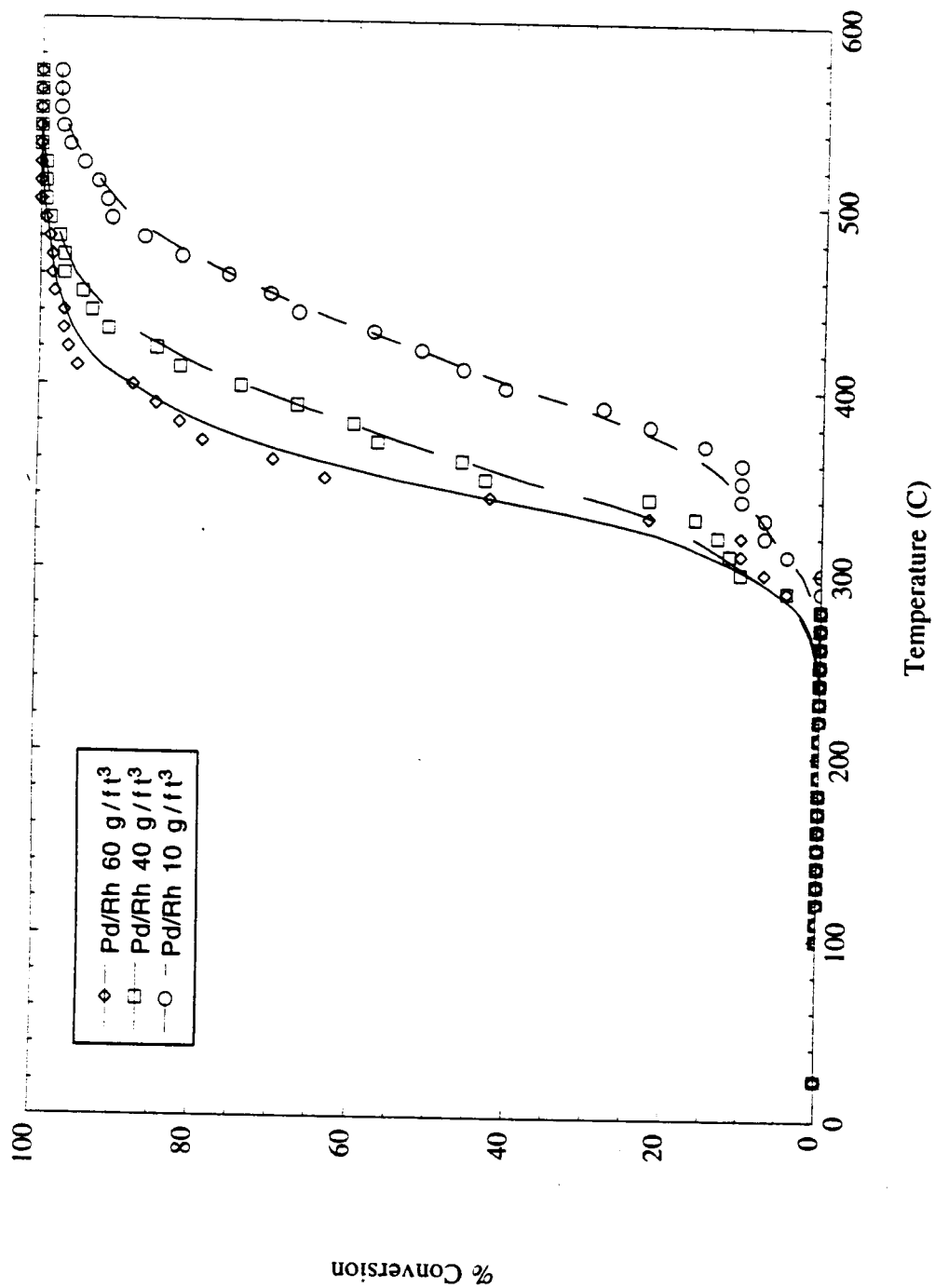


Figure 14:  $\text{CH}_4$  Conversion Efficiencies for a Fresh Catalyst with a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a Stoichiometric Cycled Lightoff Test

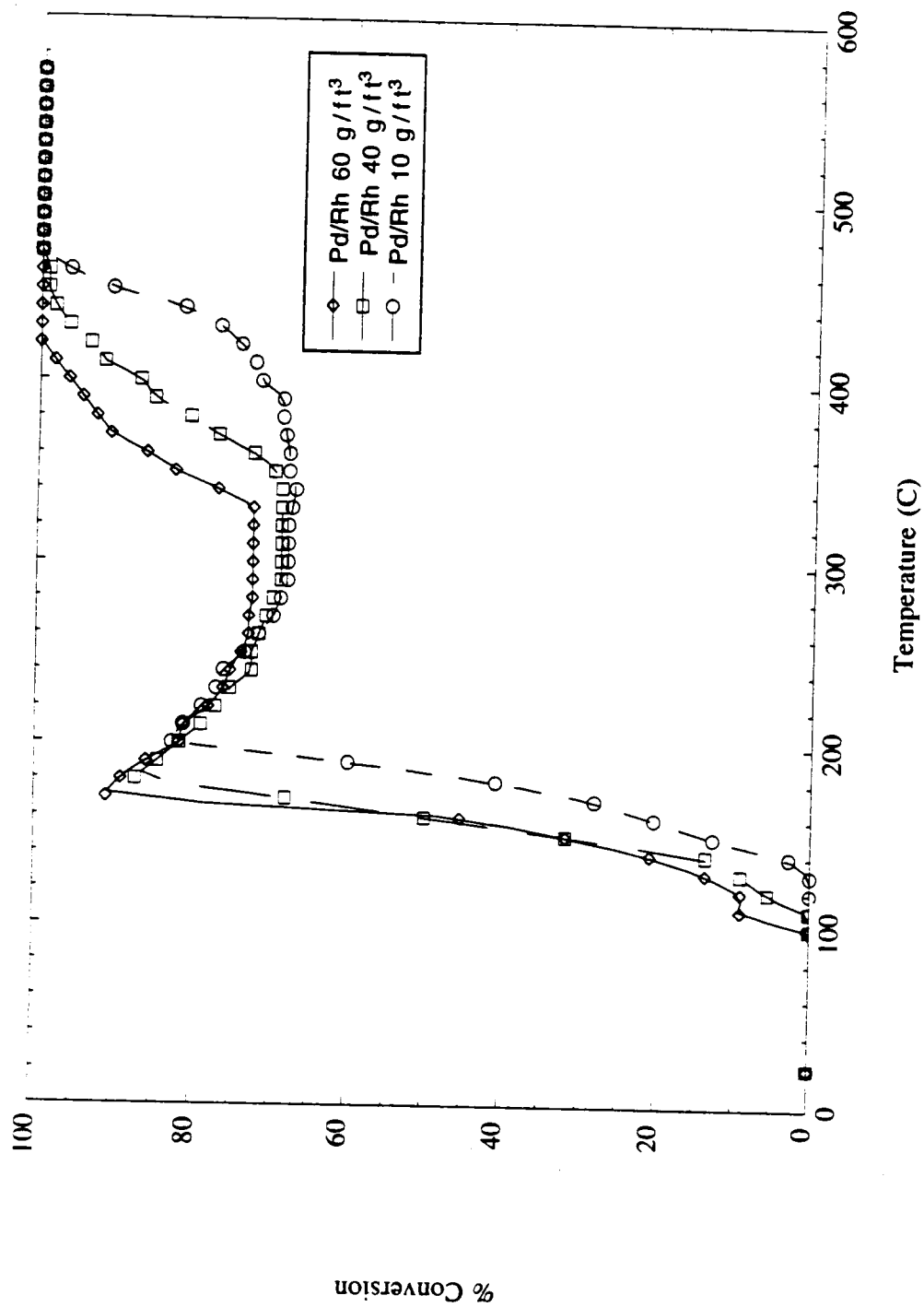


Figure 15: NO<sub>x</sub> Conversion Efficiencies for a Fresh Catalyst with a Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoichiometric Cycled Lightoff Test

the 10 g/ft<sup>3</sup> catalyst required a temperature of 190° C. Whereas, at a loadings of 40 and 60 g/ft<sup>3</sup>, light-off temperatures of approximately 162° C and 160° C, respectively, are obtained. Therefore, it can be concluded that there is virtually no change in light-off temperatures when using the 40 g/ft<sup>3</sup> as compared to the 60 g/ft<sup>3</sup> loading for the catalyst. However, the light-off temperature is decreased by 14.7% as the Pd/Rh loading is increased from 10 g/ft<sup>3</sup> to 40 g/ft<sup>3</sup>. As will be discussed in the following section, this is due to higher Pd/Rh loading resulting in larger catalytic surface areas.

#### **4.2.3 Carbon Monoxide Oxidation**

The effect of loading on the light-off behavior of CO in a cycled stoichiometric feed stream is shown in Figure 16. A light-off temperature of 178° C is obtained for the 10 g/ft<sup>3</sup> catalyst. In addition, light-off temperatures of 160° C and 155° C are found for the 40 and 60 g/ft<sup>3</sup> catalysts, respectively. A comparison of the 40 and 60 g/ft<sup>3</sup> loadings results in a light-off temperature decrease of only 3.2%. However, when the 10 g/ft<sup>3</sup> is compared to the 60 g/ft<sup>3</sup> loading, a 13% decrease in the light-off temperature occurs. As will be discussed in the next section, lower light-off temperatures result for higher Pd/Rh loadings due to the increased number of available active sites.

#### **4.2.4 Effects of Loading on the Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO**

As mentioned in Chapter 2, the advantage of having palladium and rhodium metals on the catalyst surface is that these metals have the capability of simultaneously converting significant quantities of CH<sub>4</sub>, NO<sub>x</sub> and CO. Thus, higher loadings of these precious metals result in an increase in surface area and subsequently an increase in the number of active sites that are necessary for the dissociation reactions to take place. For example, as can be seen in Figure 17, higher amounts of Pd/Rh lead to the creation of larger surface areas and ultimately better conversion efficiencies.

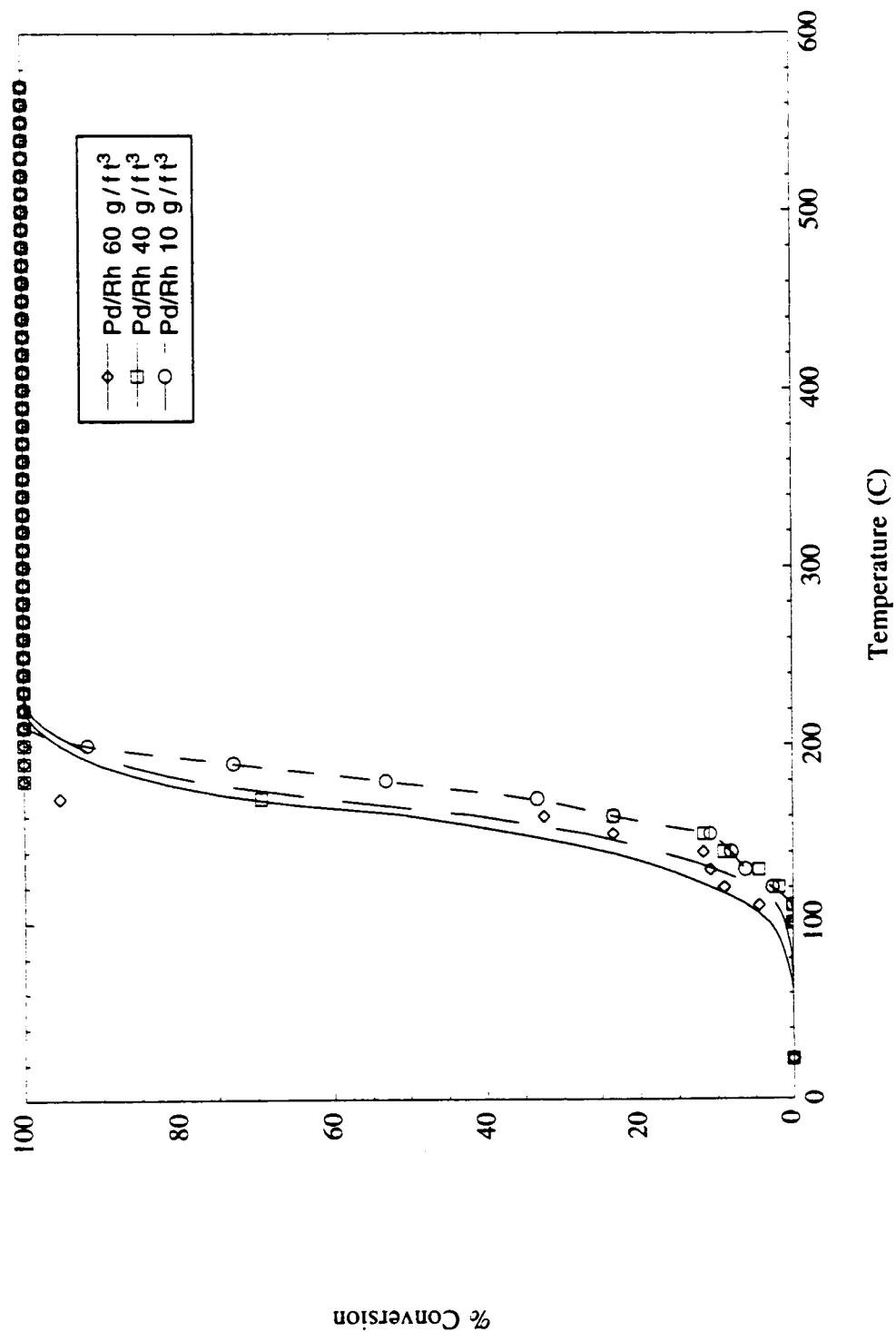


Figure 16: CO Conversion Efficiencies for a Fresh Catalyst with a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a Stoichiometric Cycled Lightoff Test

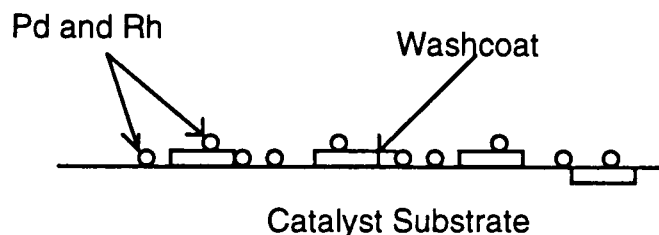


Figure 17: Palladium and Rhodium Loadings on Catalyst Substrate

The results obtained clearly demonstrate the advantages of higher loadings in the conversion efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$ . However, as seen in the Figures 15 and 16, the light-off temperature did not decrease substantially when the loading is increased from  $40 \text{ g/ft}^3$  to  $60 \text{ g/ft}^3$ .

There is a limit however to the amount of precious metal loadings that can be applied due to economic considerations and engine exhaust design limitations. For example, significantly high precious metal loadings can result in an increase in the pressure drop across the catalyst. This in turn increases the back pressure on the inlet side of the catalytic converter and subsequently affects the engine performance further upstream [31].

#### 4.3 Effects of Washcoat Composition on Conversion Efficiencies and Light-off Temperatures for $\text{CH}_4$ , $\text{NO}_x$ and $\text{CO}$

As mentioned in Chapter 2, a key component in the design of natural gas catalyst is the washcoat. Ideally, the washcoat should contain stabilizers and promoters to enhance the performance characteristics of the noble metals supported on it.

Cerium oxide,  $\text{CeO}_2$  or ceria, is a major washcoat additive for commercial three-way catalysts used for the simultaneous conversion of carbon monoxide, methane, and

nitrogen oxides in automobile exhaust. As discussed earlier, ceria aids in the degree of dispersion and stabilization of noble metals on the alumina support; it promotes the water-gas shift reaction; and it stores, releases oxygen under net-oxidizing and net-reducing conditions [23].

#### 4.3.1 Methane Oxidation as a Function of Washcoat

Although the addition of ceria to the washcoat can have the effects of enhancing the catalyst performance, the results obtained from the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat and the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat indicated otherwise in the oxidation of methane. From the results of the present investigation, the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat achieved higher conversion efficiencies and lower light-off temperatures in the lean, rich and stoichiometric feed streams. As illustrated in Figure 18 for a Pd/Rh loading of  $60 \text{ g/ft}^3$  under a noncycled lean simulation, the light-off temperature of the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat is  $387^\circ \text{C}$ . In contrast, a light-off temperature of  $450^\circ \text{C}$  is obtained for the catalyst at the same loading but with a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat. This results in a 14% decrease in the light-off temperature when the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat is used instead of the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat during lean conditions.

The characteristics for  $\text{CH}_4$  conversion in a noncycled rich simulation is shown in Figure 19. A light-off temperature of  $415^\circ \text{C}$  is obtained for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat versus  $422^\circ \text{C}$  for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat resulting in a 1.65% decrease in light-off temperature for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat. However, no change in  $\text{CH}_4$  conversion efficiency is observed for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  versus  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a cycled stoichiometric feed stream as shown in Figure 20. Although the rich and stoichiometric tests do not reveal significant light-off temperature differences in comparison to the lean feed stream, a trend can definitely be established for the reduced

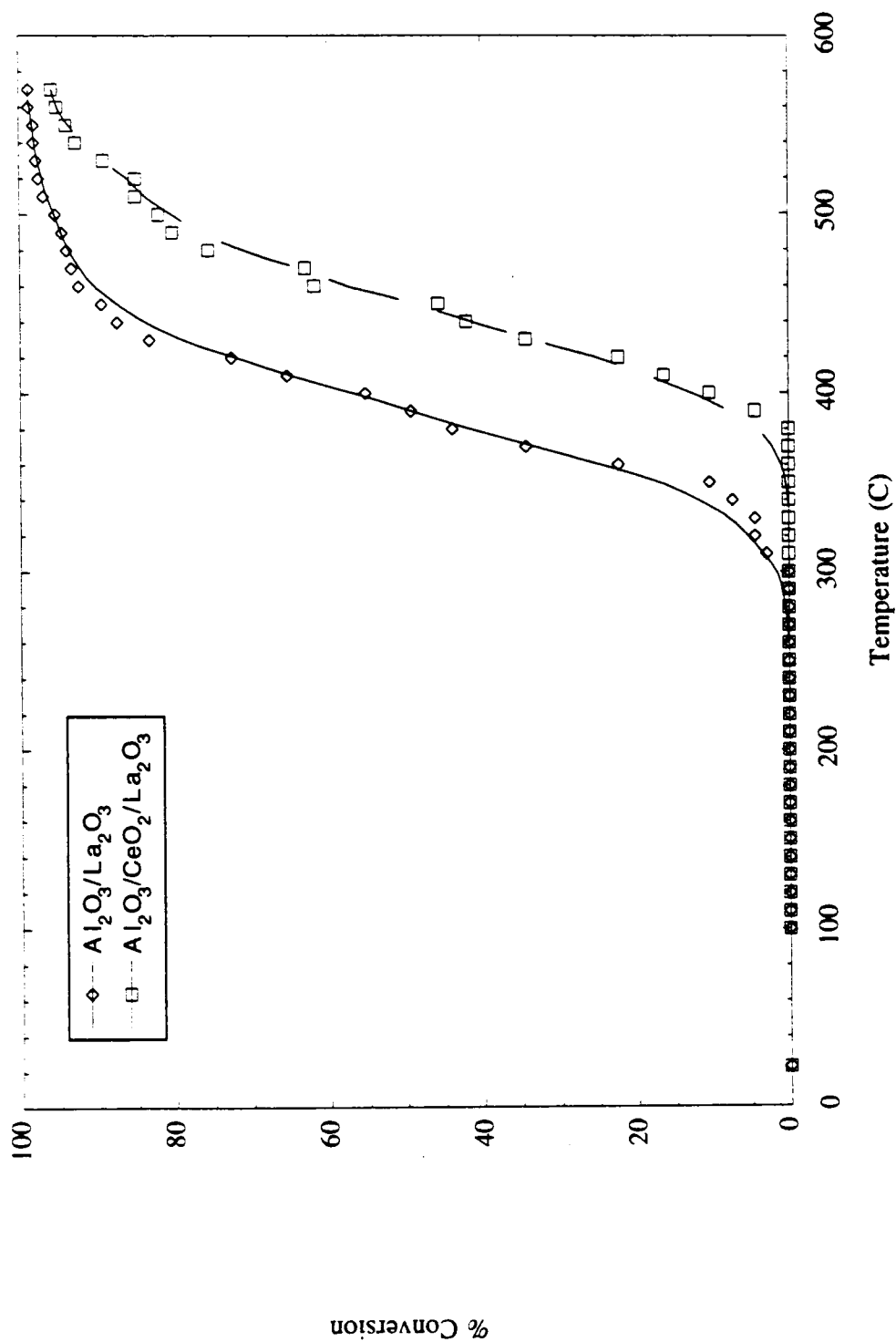


Figure 18:  $\text{CH}_4$  Conversion Efficiencies for Fresh Catalysts with  $60 \text{ g/ft}^3$  Pd/Rh loadings and  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Noncycled Lean Lightoff Test

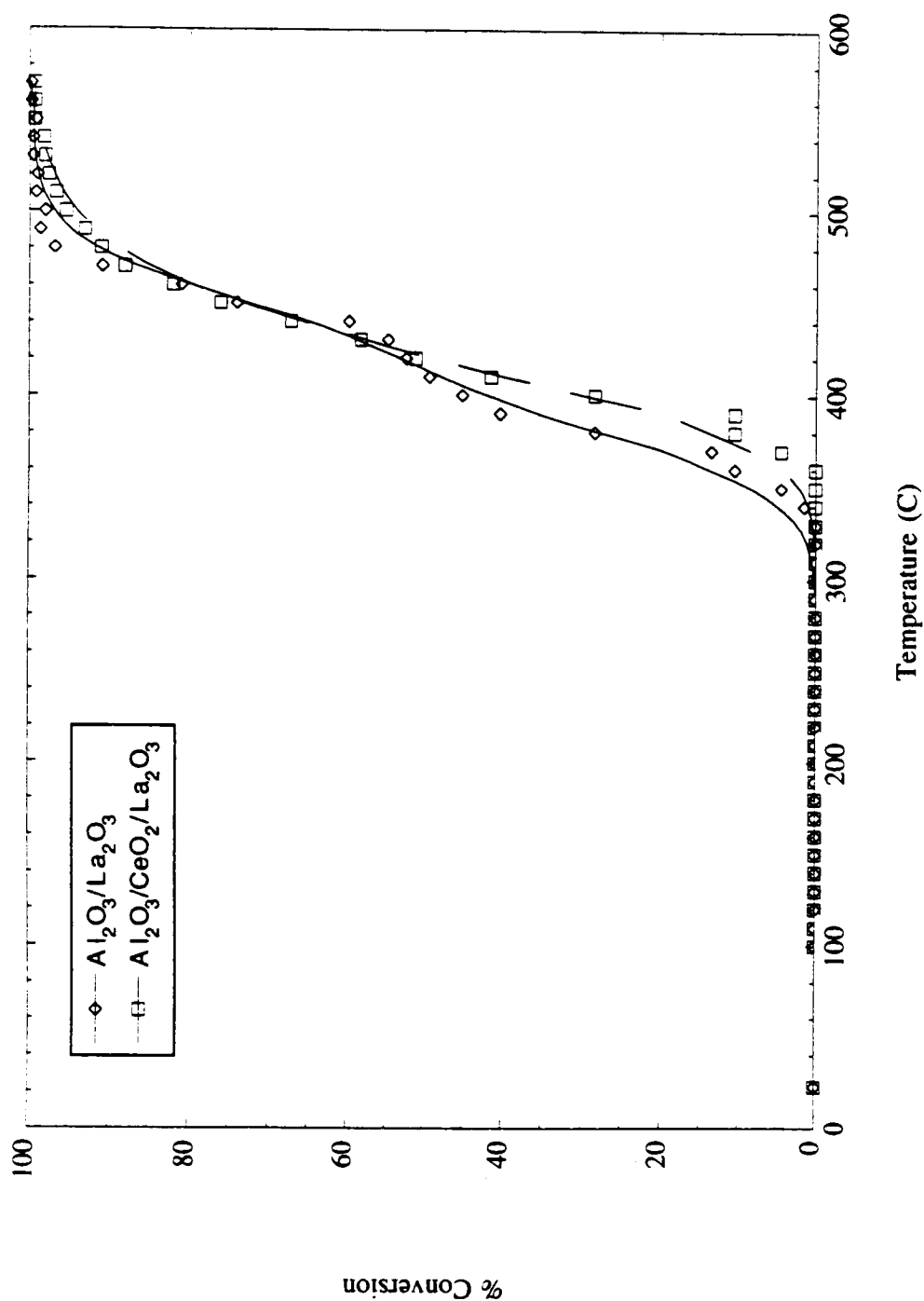


Figure 19:  $\text{CH}_4$  Conversion Efficiencies for Fresh Catalysts with 60 g/ft<sup>3</sup> Pd/Rh loadings and  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoats in a Noncycled Rich Lightoff Test

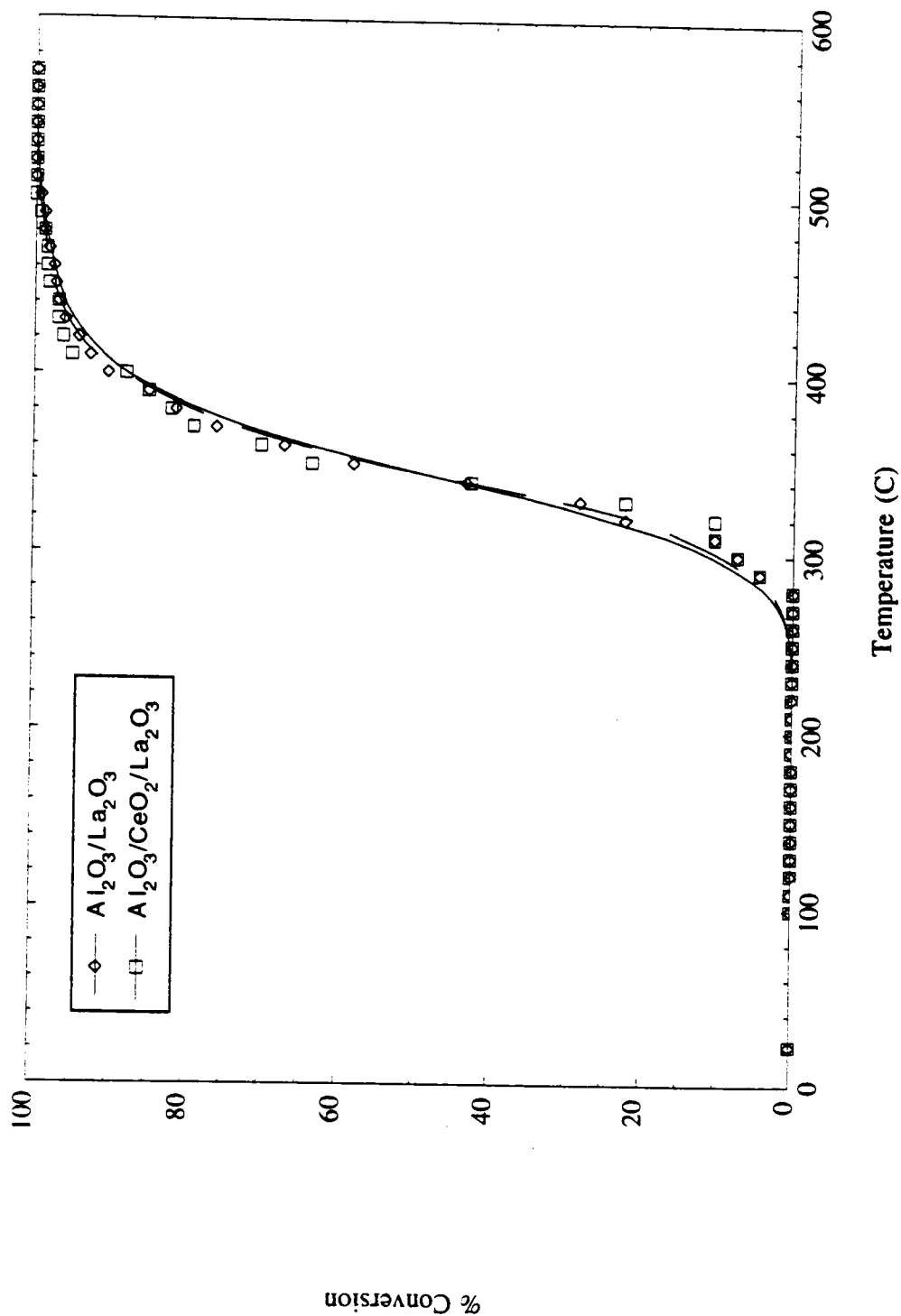


Figure 20:  $\text{CH}_4$  Conversion Efficiencies for a Fresh Catalyst with  $60 \text{ g/ft}^3$  Pd/Rh loadings and  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoats in a Cycled Stoich. Lightoff Test

conversion efficiency for the washcoat with the ceria additive as compared to the alumina/lanthana-only washcoat during the lean light-off test.

The decrease in conversion efficiency and subsequent increase in methane light-off temperatures during noncycled lean light-off test for catalyst washcoats containing ceria can be explained in the following manner. Although ceria has a much higher degree of oxygen storage capacity than alumina, the chemical kinetic reaction rates of the methane molecules must be understood. As stated earlier, the observed oxidation rate law is first-order in methane and zero-order in carbon monoxide and nitrogen oxide. In addition, the adsorption strength of the methane molecule is weaker than CO and NO<sub>x</sub>. Therefore, the resulting competition for the higher degree of available oxygen molecules in the ceria washcoat results in higher conversion efficiencies and lower light-off temperatures for the carbon monoxide and nitrogen oxide constituents for the ceria-containing washcoats. However, the methane molecules are unable to compete for the available oxygen due to the NO and CO enhanced reaction rates. This enhanced process explains the inferior conversion efficiencies of the methane molecules over the ceria additive as compared with the alumina washcoat. Although the alumina washcoat produces lower NO<sub>x</sub> and CO conversion efficiencies as will be discussed later, CH<sub>4</sub> can successfully compete for oxidation in the process and reach higher conversion efficiencies than the washcoat containing ceria.

The decreased methane conversion efficiency of alumina washcoats containing ceria compared to ceria-free alumina washcoats has also been reported by Oh, Mitchell and Siewert [1]. Their results indicated that the CH<sub>4</sub> oxidation activity of Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> under oxidizing conditions is reduced in the presence of cerium. In addition, cerium-induced suppression of the CH<sub>4</sub> oxidation activity was found to be most dramatic for the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Consequently, the activity ranking in the presence of excess O<sub>2</sub> changed from Pd > Rh > Pt without cerium to Rh > Pd ≈ Pt with cerium.

Thus, the palladium metal is found to have the best oxidation reactivity with  $\text{CH}_4$  in the cerium-free catalysts. In contrast, for catalyst containing cerium, the oxidation reactivity is highest for the rhodium metal. Therefore, for this experiment where the loading of the catalyst is in a Pd/Rh ratio of 5:1, the presence of ceria and the small amount of rhodium loading on the catalyst contributes to the lower conversion efficiencies found for the ceria containing washcoats under net-oxidizing or lean feed streams.

#### 4.3.2 $\text{NO}_x$ Reduction

The mechanism by which nitrogen oxides can be effectively reduced is dependent on the particular washcoat chosen. Figure 21 is a comparison of the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat and the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat at a Pd/Rh loading of  $10 \text{ g/ft}^3$  during a cycled stoichiometric test. Although the difference in the light-off temperatures for the two washcoats is negligible, the increased performance of the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat at elevated temperatures is more apparent. The higher  $\text{NO}_x$  conversion efficiency occurring for the ceria additive is due to the enhanced oxygen storage capacity of the ceria additive. The ceria additive has the capability to adsorb oxygen even at elevated temperatures and attributes to the subsequent reduction of nitrogen oxides in the feed stream. This is evident at a catalyst temperature of  $500^\circ\text{C}$  where the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat is able to convert 100% of the nitrogen oxides in the exhaust and the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat yields only a 76% conversion of the nitrogen oxides present. This has also been seen by Oh [20] and is due to the increased CO-NO reaction rate for catalyst with cerium additions as will be explained in the next section.

#### 4.3.3 CO Oxidation

The conversion efficiencies of CO for a fresh catalyst with a Pd/Rh loading of  $40 \text{ g/ft}^3$  and a  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a cycled stoichiometric

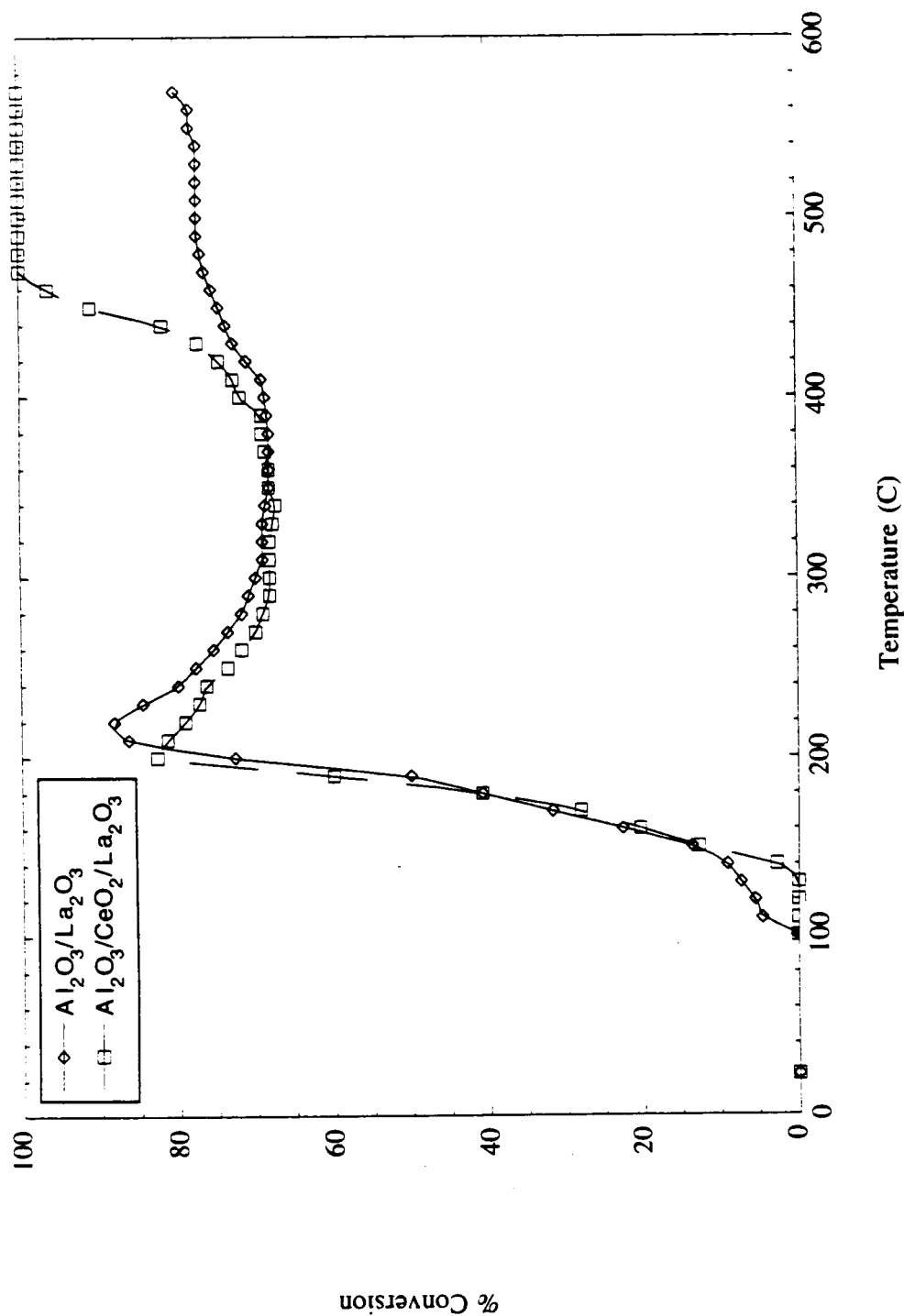


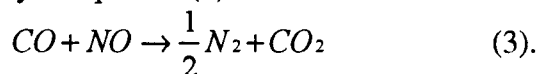
Figure 21: NO<sub>x</sub> Conversion Efficiencies for Fresh Catalysts with 10 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Cycled Stoich. Lightoff Test

light-off test is shown in Figure 22. As can be seen from the figure, a higher conversion efficiency is found for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat during the stoichiometric test. The light-off temperature for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat is  $195^\circ\text{C}$ , whereas for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat a light-off temperature of  $170^\circ\text{C}$  is obtained. This results in a  $23^\circ\text{C}$  temperature difference and a 12.8% light-off temperature decrease for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat.

The reason for the better conversion efficiencies found for the ceria additive is due to the oxygen-storage component influencing the dynamic behavior of the three-way catalyst under cycled stoichiometric conditions. This storage component adsorbs or reacts with the excess oxygen during excursions to the lean (net-oxidizing) side of the stoichiometric point. During rich, net-reducing, conditions, the stored oxygen would then be available for the CO oxidation reaction, which would enhance the conversion of carbon monoxide and nitrogen oxides simultaneously for the cycled stoichiometric conditions.

These results are also supported by Oh [21] where he examined the performance of alumina-supported catalyst with varying levels of cerium additives. From his experimental results, he concluded that there is indeed an increase in activation energy with increasing temperature for washcoats with the cerium additives. In contrast, cerium-free alumina washcoats were observed to have a constant activation energy throughout the same temperature range.

The enhanced oxidation rate of CO and the increased reduction rate of NO for the washcoat with the ceria addition at elevated temperatures can be attributed to the CO-NO reaction shown previously in equation (3) as



Oh and Eickel [20] found similar results for the enhanced oxidation of CO for washcoats containing cerium. The oxidation of CO shown previously in equation (6) is

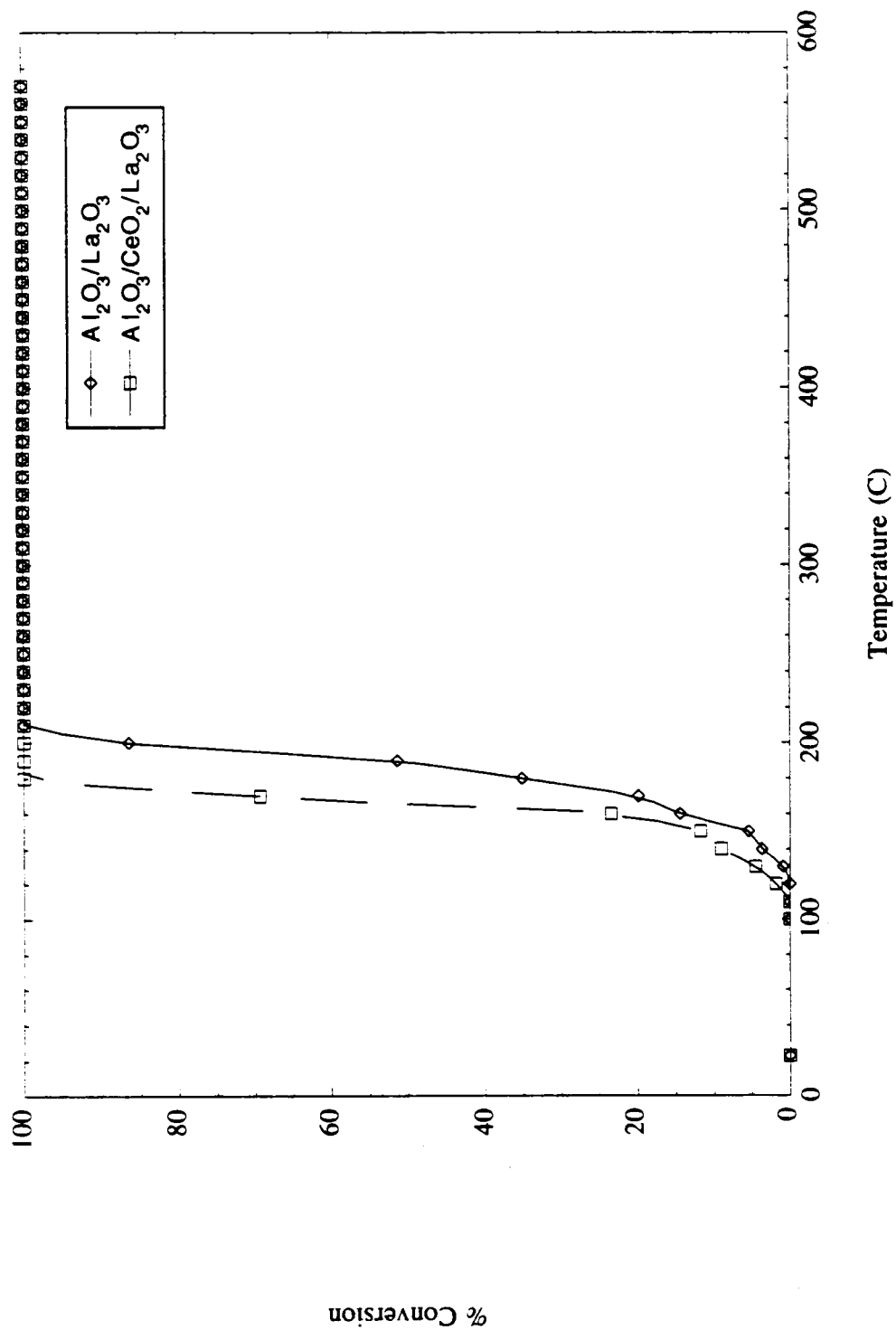
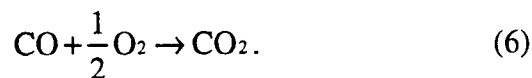


Figure 22: CO Conversion Efficiencies for Fresh Catalysts with 40 g/ft<sup>3</sup> Pd/Rh loadings and a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Cycled Stoich. Lightoff Test



Their results indicated that a higher rate of CO adsorption occurs for washcoats containing cerium additives as opposed to alumina-only washcoats.

#### 4.4 Methane's Complete Oxidation Process in Natural Gas Catalysis

As shown in Figure 23, the carbon monoxide conversion efficiency begins to decrease at a catalyst temperature of 500° C for both catalysts with Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoats during a noncycled rich light-off test. The loss in CO conversion efficiency at elevated temperatures is due primarily to the partial oxidation of methane to CO under rich, or oxygen-deficient, conditions. The detailed mechanism for methane's oxidation process is a complicated and to date not very well understood. However, the proposed reaction mechanism by Oh, Mitchell and Siewert [1] for methane oxidation can be summarized as shown in Figure 24.

The chemisorption of methane on the noble metals involves the dissociation of methane to adsorbed methyl or methylene radicals, as a result of the removal of a hydrogen atom or a hydrogen molecule from methane. The methyl or methylene then reacts with adsorbed oxygen that leads to the direct oxidation process to CO<sub>2</sub> and H<sub>2</sub>O or the formation of chemisorbed formaldehyde by methyl oxide, methyl peroxide or methylene oxide intermediates. Recent studies by Oh, Mitchell and Siewert indicate that the adsorbed formaldehyde then dissociates into adsorbed CO and adsorbed hydrogen atoms. These adsorbed CO and hydrogen atoms have been observed to either desorb as CO and H<sub>2</sub>, or react with adsorbed oxygen to produce CO<sub>2</sub> and H<sub>2</sub>O, depending on the inlet conditions of the feed stream and the catalyst temperature.

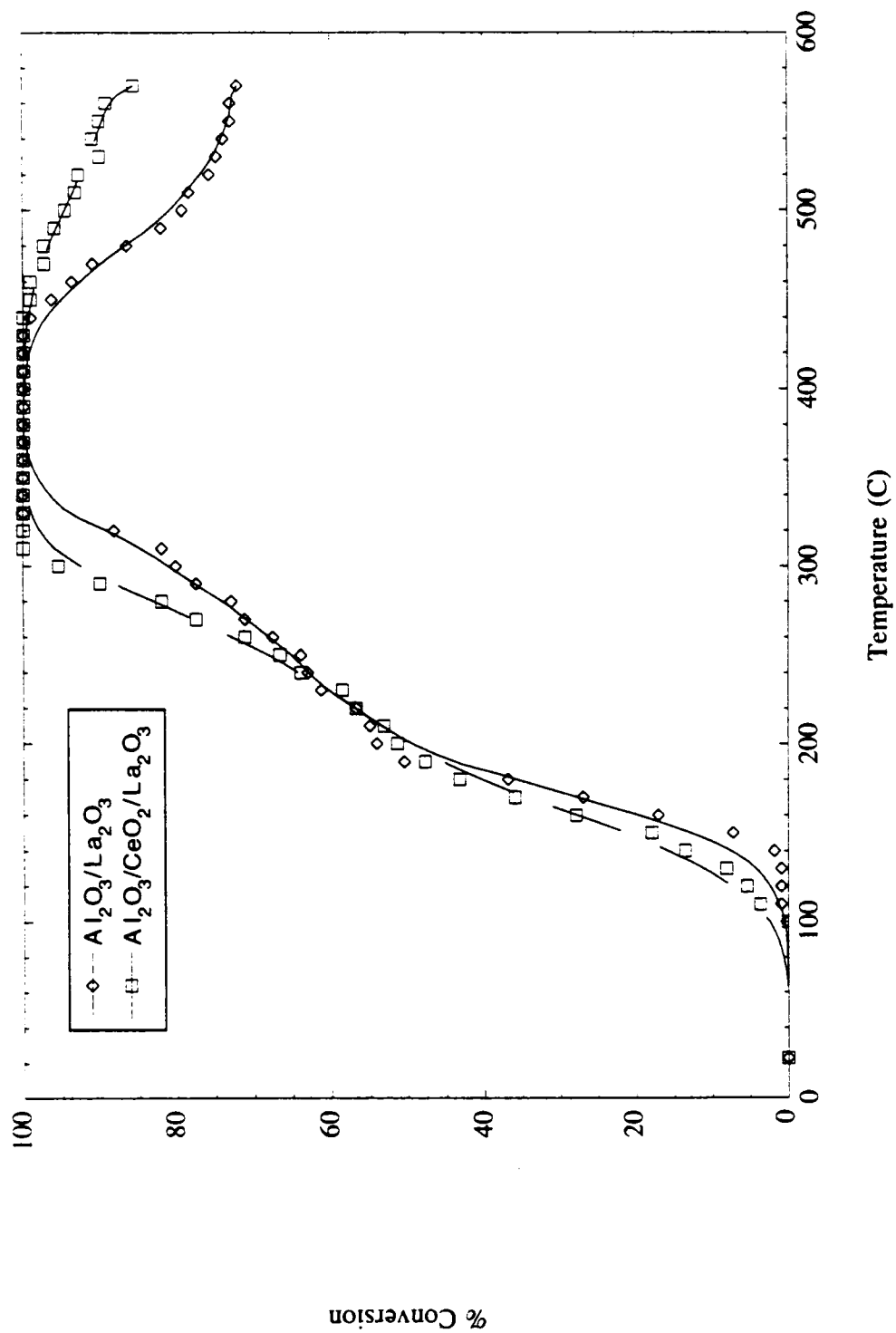


Figure 23: CO Conversion Efficiencies for Fresh Catalysts with 60 g/ft<sup>3</sup> Pd/Rh loadings and  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoats in Noncycled Rich Lightoff Tests

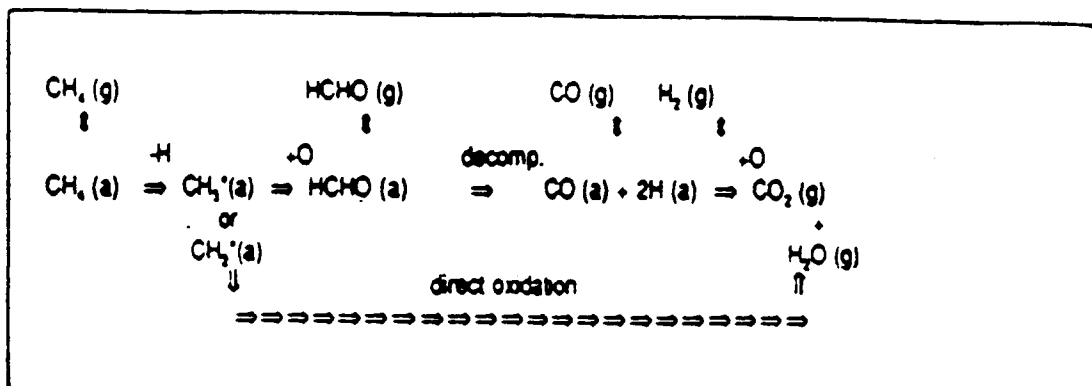


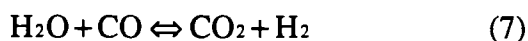
Figure 24: Oxidation of Methane under Rich Conditions

Based on this reasoning, the decrease in CO conversion efficiencies at elevated temperatures as seen in Figure 23 for the rich case is due primarily to the partial oxidation of methane to formaldehyde and subsequently to desorbed carbon monoxide under oxygen-deficient conditions.

In comparing the loss of conversion efficiency for the two washcoats, note the advantage of the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in achieving less partial oxidation of methane to carbon monoxide. This is due to ceria's oxygen storage capability as discussed previously. The oxygen storage capacity of the ceria additive results in an enhancement of the CO oxidation process and thus higher CO conversion efficiencies as compared to the ceria-free washcoat.

#### 4.5 Effects of the Water-Gas Shift Reaction and Steam Reforming Reaction on Carbon Monoxide and Methane Conversion Efficiencies

The effects of the water-gas shift reaction on the constituents in the exhaust feed stream of a NGV is of particular interest since the NGV exhaust typically containing large amounts of water vapor on a volumetric basis. The water-gas shift reaction is shown below in equation (7):



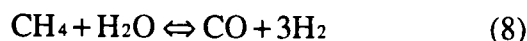
One important criteria to understanding the catalysis of natural gas is establishing the degree in which the water-gas shift reaction plays in oxidizing the carbon monoxide constituent. As stated earlier, natural gas vehicle exhaust contains large amounts of water vapor and it could be concluded that the large presence of water vapor would drive the water-gas shift reaction to oxidize carbon monoxide. However, carbon dioxide is also very prevalent in the exhaust and thus the formation of carbon monoxide from  $\text{CO}_2$  cannot be ruled out.

By the natural gas simulation scheme used in the present study, the amount of water vapor and carbon dioxide occurring for both of these constituents in the feed stream is 10% by volume for the lean, rich and stoichiometric operating conditions. Therefore, it could be concluded that the water-gas shift reaction would not play a major role in the oxidation or formation of carbon monoxide as a result of these offsetting constituents. However, one must also examine the subsequent formation of these constituents based on the feed stream inlet conditions.

The water-gas shift reaction over platinum, palladium and rhodium catalysts with alumina washcoats under net-reducing, or fuel rich conditions, has been investigated [1]. The conversion of the constituents were closely monitored during processes with and without the addition of carbon dioxide to the feed stream. The results suggested that CO

produced over either Pt/Al<sub>2</sub>O<sub>3</sub> or Pd/Al<sub>2</sub>O<sub>3</sub> was virtually unaffected by the CO<sub>2</sub> addition. Further, over the palladium and platinum catalyst, the addition of CO<sub>2</sub> to the feed stream had little impact on the oxidation of methane. However, for the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst the increasing level of CO<sub>2</sub> tended to increase the level of CO production during methane oxidation. This suggested that the water-gas shift reaction played a significant role in determining the reactions occurring over the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst, but not over Pt/Al<sub>2</sub>O<sub>3</sub> or Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. Therefore, it can be concluded that the combination of precious metals in the Pd/Rh catalyst used in this research must take into account the effect of the water-gas shift reaction in the oxidation of methane particularly under net reducing conditions.

According to the literature on natural gas catalysis, the steam reforming reaction shown in equation (8)



assists in the oxidation of methane only in small amounts [13,33].

Both the water-gas shift reaction and the steam reforming reaction are highly dependent on the temperature of the catalyst and play a significant role in catalysis only at low and elevated temperatures of the catalyst's operating range. However, as stated earlier in Chapter 2, the majority of emissions occur before the catalyst reaches light-off temperatures during the initial start-up; therefore, any reduction of the CH<sub>4</sub> or CO constituents in the feed stream should be considered.

#### **4.6 Effects of Aging on Catalyst Performance and Durability**

Up to this point, the comparative discussion of catalyst performance has been limited to fresh catalyst; however, the durability and degradation of the catalyst over time

is an important consideration in over-all effectiveness of the catalyst in commercial applications. As mentioned in Chapter 2, the stability of methane in the feed stream requires catalysts operating at elevated temperatures in order to ensure necessary conversions. Therefore, the ability of the catalyst to withstand high temperatures becomes a critical factor in the performance design of the catalyst. Moreover, the requirement for automobile catalyst to reduce vehicle emissions to within legislated standards over 100,000 miles also places an emphasis on the rate of catalyst deactivation during use.

The durability and degree of degradation of the catalyst are a function of several parameters such as the type of precious metal loading on the catalyst, the amount of loading, and the type of washcoat chosen. Therefore, it can be shown that the effects of aging on these parameters can significantly degrade the performance of a catalyst in converting  $\text{CH}_4$ ,  $\text{NO}_x$  and CO constituents in the NGV simulated exhaust.

In this study, the degradation of performance of six different catalyst is investigated with Pd/Rh loadings of 10 and 60 g/ft<sup>3</sup>. The washcoats chosen for the catalysts consist of  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  blends. The catalysts are aged as stated in Chapter 3 by flowing an alternating feed stream of 5%  $\text{O}_2/\text{N}_2$  and 5%  $\text{H}_2/\text{N}_2$  across the catalyst at 0.8 liters/min with a surrounding temperature of 1000° C.

These catalysts are evaluated based on their performance under rich noncycled, lean noncycled and stoichiometric cycled natural gas exhaust simulations. In addition, since the fresh catalysts are tested under the same feed stream conditions, a comparison of fresh versus thermally aged catalyst can be discussed.

#### 4.6.1 CH<sub>4</sub> Conversion Efficiency as a Function of Loading and Washcoat

##### Loading Effects

The effects of aging and the subsequent degradation of the catalyst over time in converting methane in a cycled stoichiometric feed stream are shown in Figure 25. The light-off temperature for the catalyst with an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat at a loading of 60 g/ft<sup>3</sup> increases from 345° C to 440° C as a result of the aging process. This results in an increase of 21.6% in the light-off temperature.

Also shown in Figure 25 is the effect of aging on catalyst with a loading of 10 g/ft<sup>3</sup> and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat during a cycled stoichiometric light-off test. In comparison with a fresh catalyst at the same loading and washcoat, a light-off temperature of 415° C is observed for the fresh catalyst and 522° C for the aged catalyst. This results in an increase of 20.5% in the light-off temperature for the aged catalyst in a cycled stoichiometric feed stream.

As can be seen from these results, the light-off temperatures for the 10 and 60 g/ft<sup>3</sup> aged catalysts have been increased by the same percentage due to the aging process. However, the performance of the catalysts at elevated temperatures reveals a higher degree of conversion efficiency loss for the 10 g/ft<sup>3</sup> versus the 60 g/ft<sup>3</sup> sample. At a catalyst temperature of 570° C, the maximum conversion efficiency of the fresh 60 g/ft<sup>3</sup> catalyst is 100% and is reduced to 94% as a result of aging. Whereas, for the 10 g/ft<sup>3</sup> sample, the fresh sample has a maximum conversion of 88% at 570° C and is reduced to 72% after the aging process. Therefore, at elevated temperatures a higher degree of thermal degradation is apparent for the catalyst containing a lower loading of Pd/Rh.

In a noncycled rich feed stream the effect of aging on the loss of performance of lower loading catalysts is more dramatic. As shown in Figure 26, the light-off temperature increased from 415° C for the fresh catalyst to 510° C for the aged catalyst resulting in an

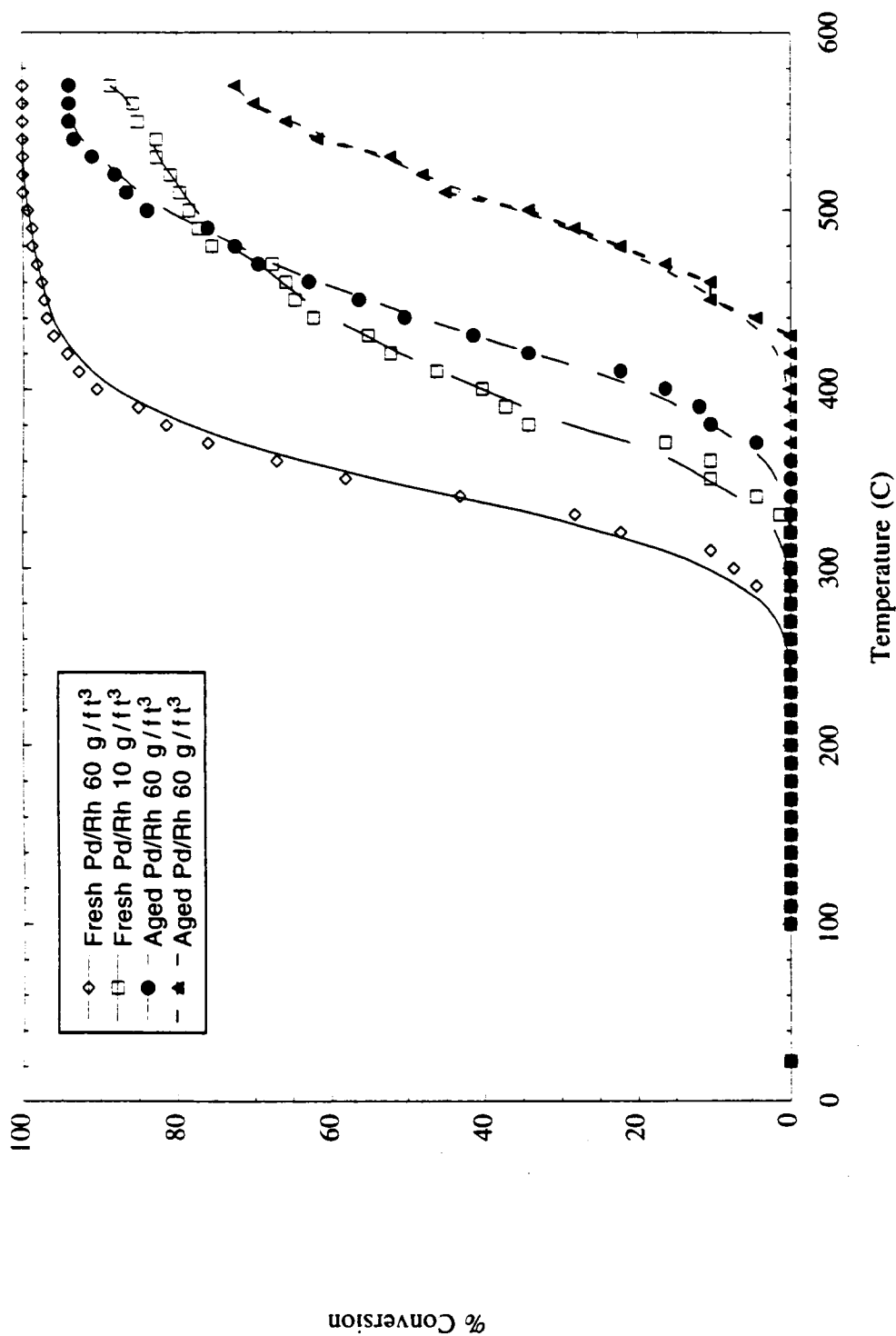


Figure 25: CH<sub>4</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Cycled Stoich. Lightoff Tests

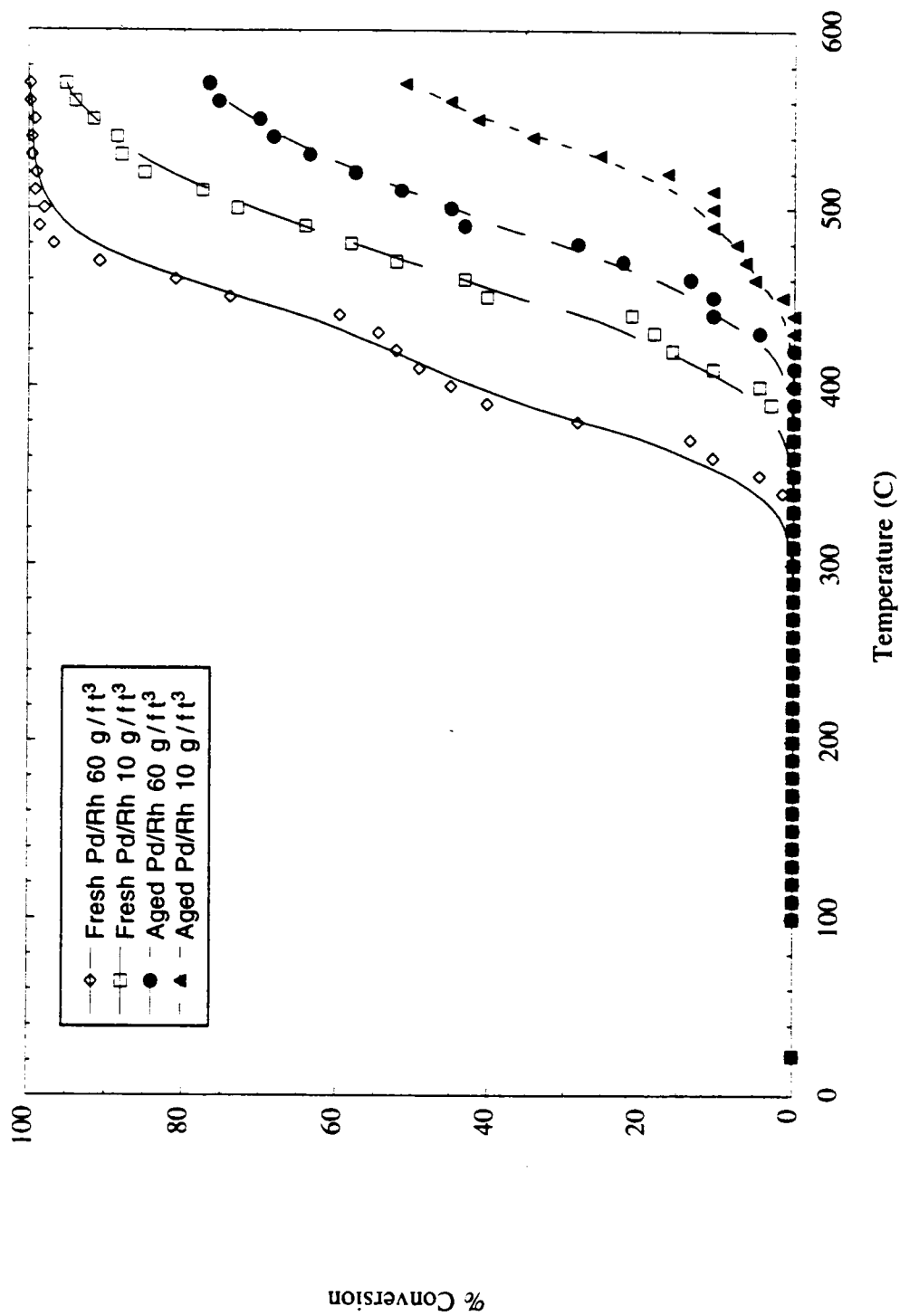


Figure 26: CH<sub>4</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Noncycled Rich Lightoff Tests

increase of 22.8% in the light-off temperature. On the other hand, the 10 g/ft<sup>3</sup> catalyst is able to convert 50% of the methane in the feed stream only at an elevated temperature of 570° C.

The loss of performance due to thermal degradation is more dramatic at elevated temperatures. At a temperature of 570° C, the 60 g/ft<sup>3</sup> has a maximum conversion capability of 100% in the fresh state and a 77% conversion efficiency for the aged catalyst resulting in a 23% loss due to thermal degradation. On the other hand, the 10 g/ft<sup>3</sup> sample yields a maximum conversion of 95% at 570° C in the fresh state and a 50% conversion efficiency as a result of aging. Therefore, a 45% loss of the conversion capability is incurred by the 10 g/ft<sup>3</sup> sample as compared to a loss of only 23% for the 60 g/ft<sup>3</sup> catalyst sample.

Results obtained from the noncycled lean simulation exhibit a trend similar to the noncycled rich feed stream. As shown in Figure 27, the light-off temperature is 380° C for the fresh catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat, whereas the light-off temperature for the aged sample is 520° C under the same conditions. This results in a light-off temperature increase of 39% for the aged catalyst. For the fresh versus aged 10 g/ft<sup>3</sup> samples, the maximum conversion efficiency for the aged sample is 40% at a catalyst temperature of 570° C as compared to the fresh catalyst's ability to convert 92% of the methane at the same temperature. This results in a 52% loss of conversion capability as a result of thermal degradation on the 10 g/ft<sup>3</sup> sample in contrast to a 27% loss of conversion found for the 60 g/ft<sup>3</sup> catalyst sample.

In light of these results, it can be concluded that there is indeed a correlation between the degree of thermal degradation that takes place in the catalyst and the amount of precious metal loading present. These conclusions have also been found by Muraki and Sobukawa [22]. Their results indicated that the light-off durability performance of the catalyst improved with increased Pd/Rh loadings. They compared the fresh versus aged

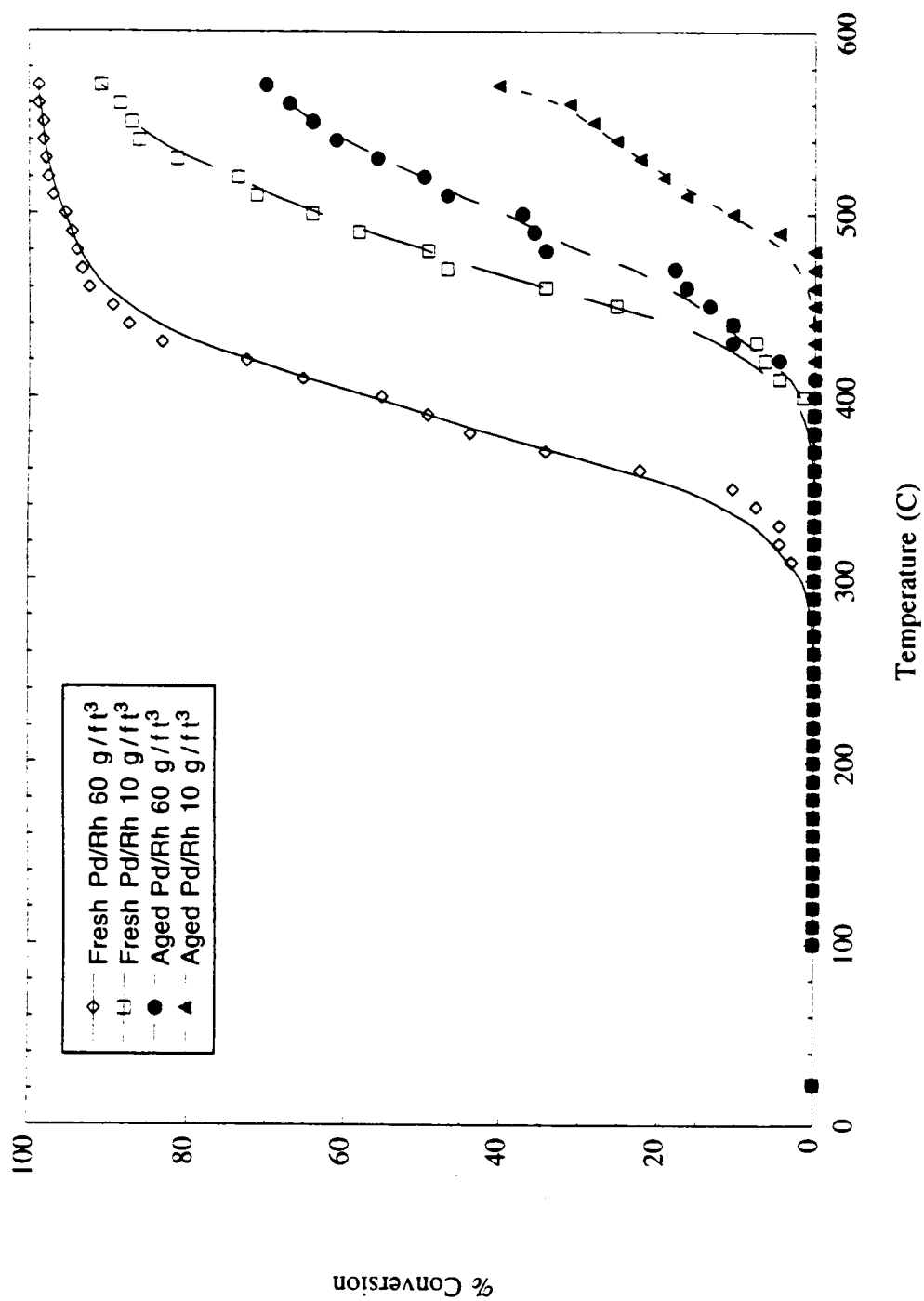


Figure 27: CH<sub>4</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Noncycled Lean Lightoff Tests

light-off temperatures for the two different loadings of 20 and 40 g/ft<sup>3</sup>. The light-off temperature for the catalyst with a Pd/Rh loading of 20 g/ft<sup>3</sup> was found to increase much more significantly after aging than the catalyst with a 40 g/ft<sup>3</sup> loading. Therefore, they concluded that the degree of thermal degradation and the effect on the light-off temperatures and conversion efficiencies of the catalysts was a function of the amount of loading on the catalysts.

### **Washcoat Effects**

The effects on methane conversion as a function of the addition of ceria to the washcoat is shown previously in section 4.3.1 for fresh catalysts. The purpose of this section is to investigate the effects of aging and thermal degradation on the washcoat with and without the ceria additive and the corresponding methane conversion efficiencies.

The most dramatic result of thermal degradation as a result of the addition of ceria to the washcoat can be seen in Figure 28. At a Pd/Rh loading of 60 g/ft<sup>3</sup> and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat, the light-off temperature is 510° C during a noncycled rich feed stream. In comparison, the light-off temperature for the Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat corresponding to the same loading and under the same feed stream conditions cannot be shown due to the catalyst's inability to convert 50% of the methane in the feed stream. A maximum conversion of 10% is achieved only after the catalyst temperature has reached 570° C.

The higher degree of thermal degradation in the catalysts containing ceria has also been found by Theis, Casarella and Mahan [23] and will be explained further in the next section.

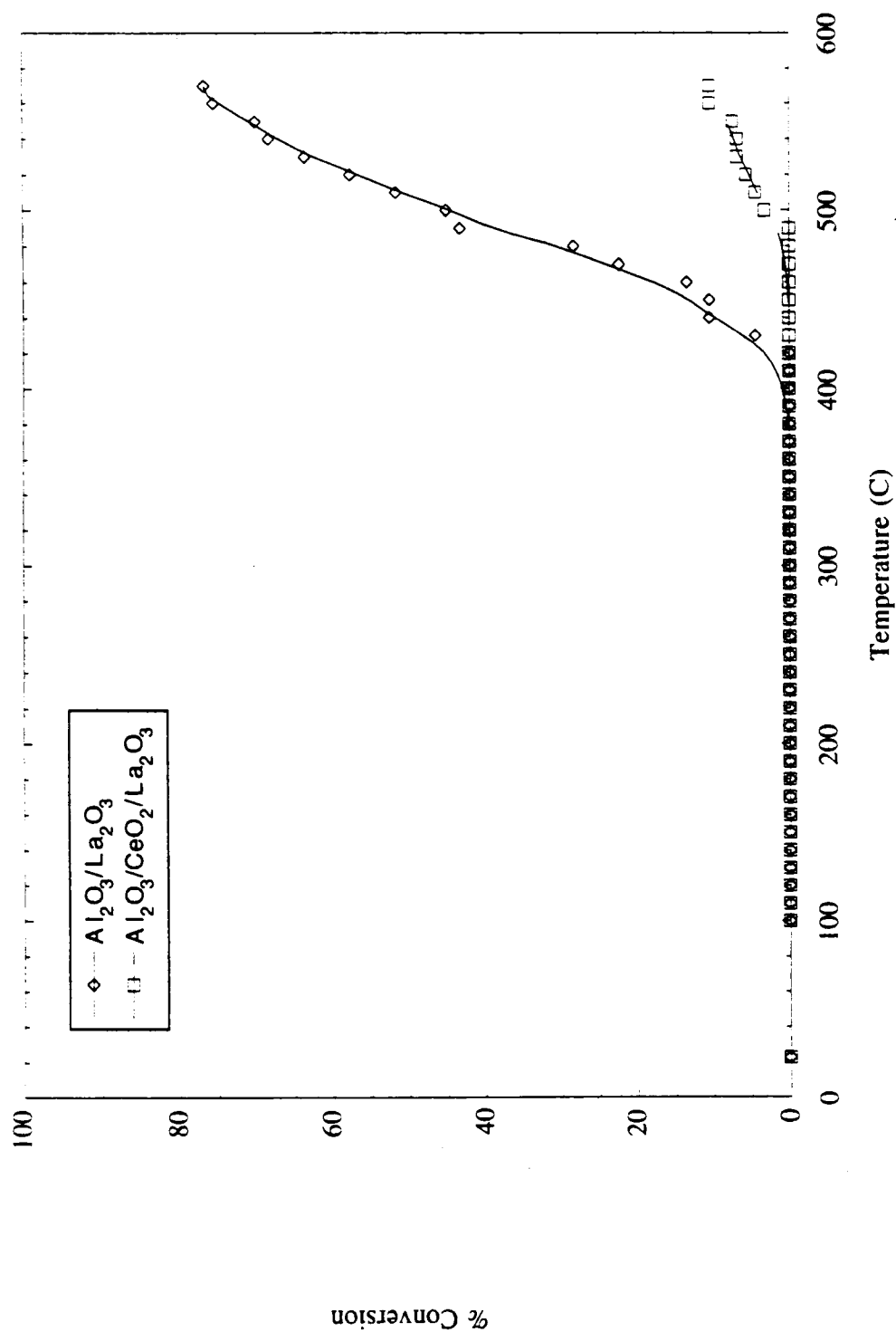


Figure 28:  $\text{CH}_4$  Conversion Efficiencies for Aged Catalysts with 60 g/ft<sup>3</sup> Pd/Rh loadings and  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Noncycled Rich Lightoff Test

## 4.6.2 NO<sub>x</sub> Conversion Efficiency as a Function of Loading and Washcoat

### Loading Effects

By using catalysts with the same washcoat but with different loadings, the effects of thermal degradation on NO<sub>x</sub> conversion efficiency can be investigated. The light-off temperatures obtained from Figure 29 illustrate the effect of this thermal degradation during a noncycled rich feed stream. For the aged catalyst with 60 g/ft<sup>3</sup> loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat the light-off temperature is 200° C. This is compared to the fresh catalyst's light-off temperature of 140° C under the same conditions as the aged catalyst. Therefore, a 42.9% increase in light-off temperature for NO<sub>x</sub> conversion occurs in the noncycled rich feed stream as a result of the thermal degradation experienced by the catalyst during the aging process. Figure 29 also gives a light-off temperature for the aged 10 g/ft<sup>3</sup> catalyst as 235° C compared to 175° C for the fresh catalyst with the same washcoat and loading. This results in a 34% increase in the light-off temperature for the fresh versus aged catalyst with a Pd/Rh loading of 10g/ft<sup>3</sup> and a Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat.

One of the reasons for the significant loss of the conversion capability of the catalyst is due to the sintering of the palladium and rhodium metals on the catalyst. As will be discussed further in the next section, this sintering leads to decreased catalytic activity and therefore reduced conversion capabilities.

### Washcoat Effects

By comparing the Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat and the Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat, an interesting development emerges. As discussed previously in section 4.3.2, the NO<sub>x</sub> light-off temperature curves for fresh catalysts with Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoats did not exhibit any distinguishing trend for adequate comparison. However, the performance of the washcoat with the ceria additive did yield

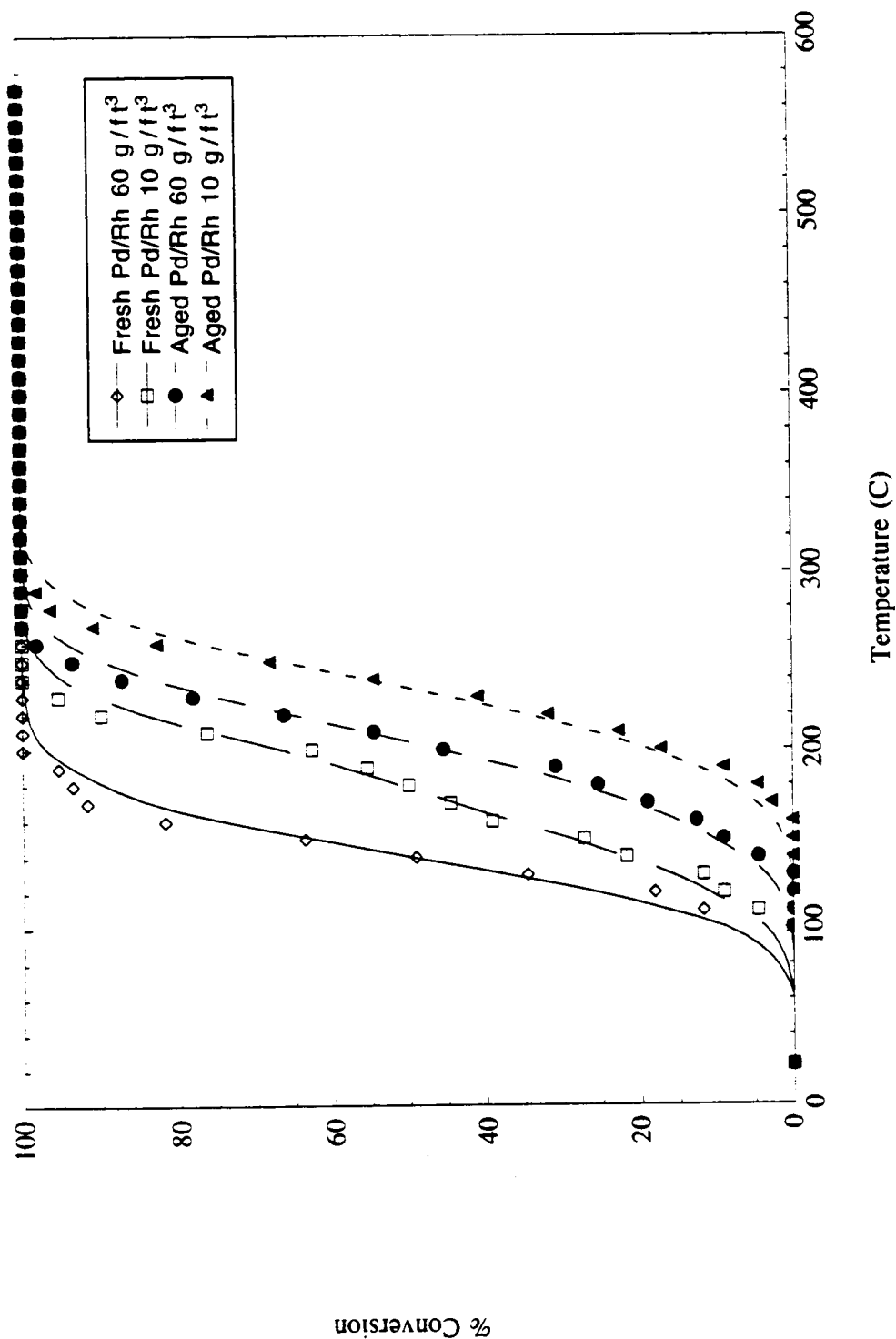


Figure 29: NO<sub>x</sub> Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Noncycled Rich Lightoff Tests

higher conversion efficiencies at elevated temperatures during a cycled stoichiometric feed stream, and hence the ceria additive became an essential ingredient in the washcoat design configuration for maximizing  $\text{NO}_x$  conversion efficiencies.

However, for aged catalysts with either an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat or an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat the opposite trend is found. As seen in Figure 30 during a cycled stoichiometric feed stream, not only are the light-off temperatures for the washcoat containing the ceria additive higher than the corresponding  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat, the conversions for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat are significantly lower than the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat at elevated temperatures. For a loading of  $60 \text{ g/ft}^3$  and an aged  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat, the light-off temperature is  $195^\circ \text{C}$  compared to  $205^\circ \text{C}$  for the aged catalyst having a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat. Similarly, the catalysts with a loading of  $10 \text{ g/ft}^3$  yields a light-off temperature of  $237^\circ \text{C}$  for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat and a  $250^\circ \text{C}$  light-off temperature for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat. This results in a 5.1% increase in light-off temperature for the  $60 \text{ g/ft}^3$  catalysts and a light-off temperature increase of 5.5% for the  $10 \text{ g/ft}^3$  catalyst.

Although the light-off temperature comparisons may not illustrate vast differences, the interesting conversion behavior occurs at elevated temperatures as seen from Figure 30. At a catalyst temperature of  $500^\circ \text{C}$  and a loading of  $60 \text{ g/ft}^3$ , the conversion efficiency for the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat catalyst is 97% as compared 83% for the catalyst with a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat. Correspondingly, the washcoat with a Pd/Rh loading of  $10 \text{ g/ft}^3$  yields 67% conversion for  $\text{NO}_x$  at a temperature of  $500^\circ \text{C}$  compared with a 53% conversion achieved for the catalyst containing a  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat at the same temperature.

The trend is primarily due to the higher degree of thermal degradation occurring for the catalyst containing the ceria addition. As will be discussed in the next section, the

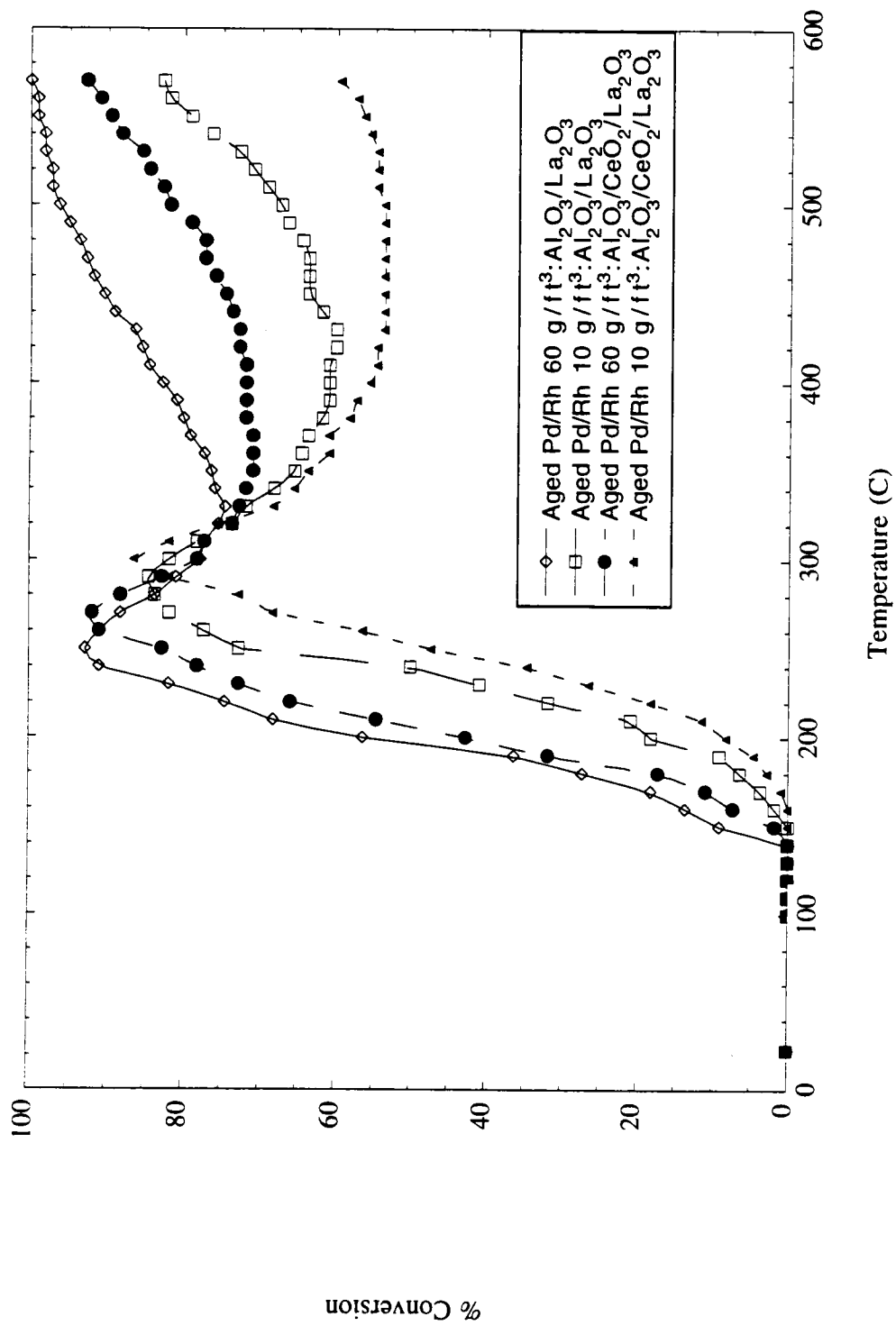


Figure 30: NO<sub>x</sub> Conversion Efficiencies for Aged Catalysts with 10 and 60 g/t<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Cycled Stoich. Lightoff Test

reduced conversion capability of the catalysts is due to the sintering of the washcoat and the thermal interactions between the washcoat and the precious metal loading.

#### **4.6.3 CO Conversion Efficiency as a Function of Loading and Washcoat**

##### **Loading Effects**

The detrimental effects of aging on the conversion efficiency of carbon monoxide is illustrated in Figure 31. The light-off temperature for the aged catalyst with an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat and a  $60 \text{ g/ft}^3$  Pd/Rh loading is  $280^\circ \text{C}$  compared to the light-off temperature of  $200^\circ \text{C}$  for the fresh catalyst with the same loading and washcoat during a rich noncycled test. This results in a 40% increase in the light-off temperature for the aged catalyst as compared with the fresh catalyst. In addition, the light-off temperature for the aged catalyst with a  $10 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat is  $310^\circ \text{C}$ , whereas the fresh catalyst yields a light-off temperature of  $220^\circ \text{C}$ . This results in a light-off temperature increase of 40.9% for the aged catalyst. It is also apparent that there is a significant reduction in the conversion capabilities of the aged catalyst at elevated temperatures. For instance, as seen in Figure 31, at a temperature of  $400^\circ \text{C}$  the CO conversion efficiencies for both the 10 and  $60 \text{ g/ft}^3$  fresh catalyst are 100%. However, after aging, the conversion efficiencies for the 10 and  $60 \text{ g/ft}^3$  are 54% and 53%, respectively. This demonstrates that their corresponding conversion efficiencies are practically indistinguishable at temperatures above  $320^\circ \text{C}$ . Therefore, it is concluded that the added benefits of higher Pd/Rh loadings on the catalyst are not significant contributors to carbon monoxide conversion efficiencies at elevated temperatures. This drop in conversion efficiency for the aged catalysts provides an in depth look at the capability of the catalyst to convert carbon monoxide over time and its reduced performance at elevated temperatures regardless of higher Pd/Rh loadings.

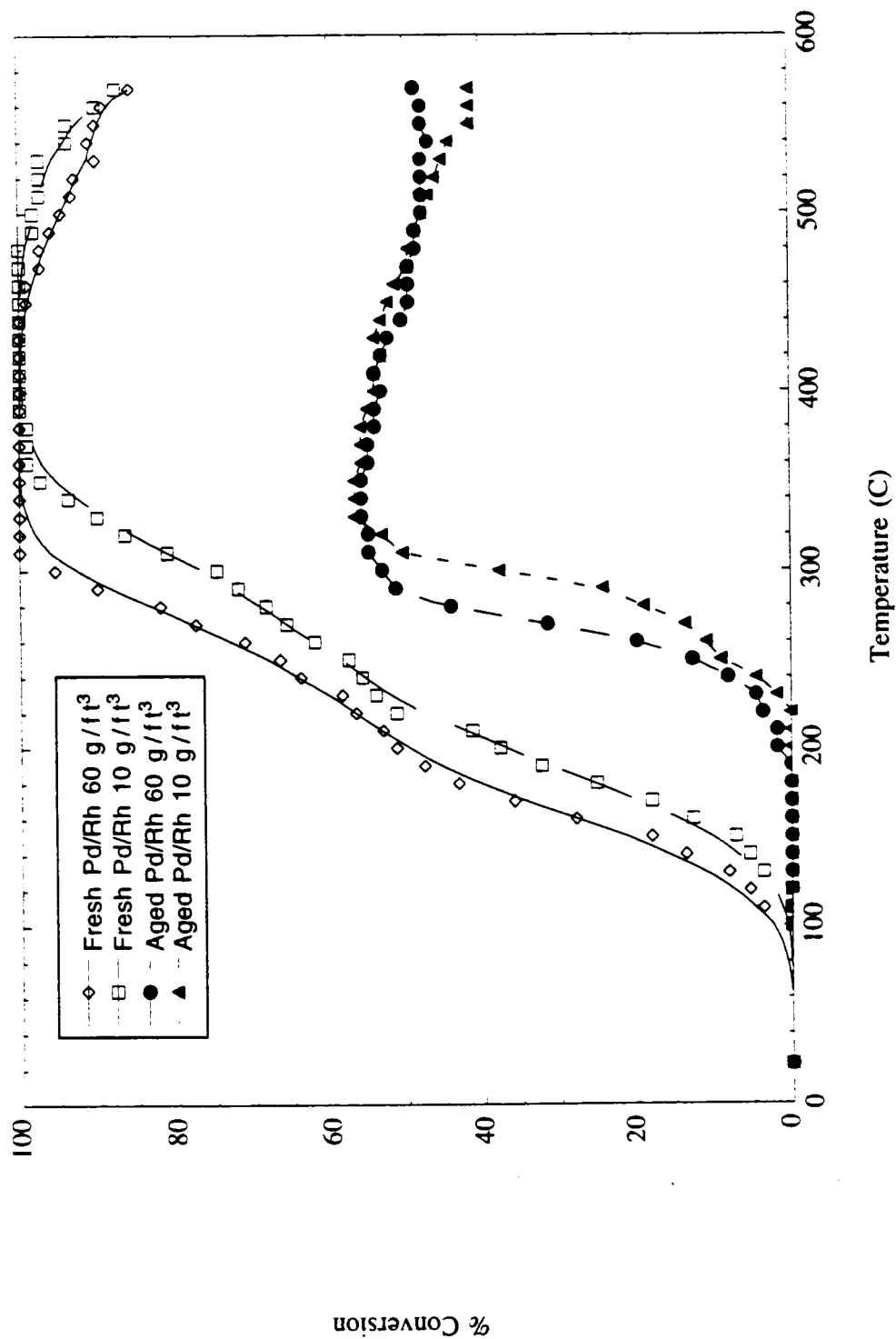


Figure 31: CO Conversion Efficiencies for Fresh and Aged Catalysts with 10 and 60 g/ft<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Noncycled Rich Lightoff Tests

## Washcoat Effects

As seen earlier, the conversion efficiencies of  $\text{CH}_4$  and  $\text{NO}_x$  are reduced with aged catalysts containing the ceria additive. For the conversion of carbon monoxide in the feed stream, a similar trend is observed. As seen in Figure 32, no difference is perceived in the light-off temperatures between the catalyst with and without the ceria additive for both the 60 and 10  $\text{g/ft}^3$  Pd/Rh loadings during a noncycled rich feed stream simulation. However, as the catalyst temperature is increased, a significant drop in the carbon monoxide conversion capability is experienced by the washcoat with the ceria additive. For example, at a catalyst temperature of  $500^\circ\text{C}$  and a loading of 60  $\text{g/ft}^3$ , the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat produces a conversion efficiency of 75%, but the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat at the same loading gives only a 47% conversion efficiency. This is also apparent at a Pd/Rh loading of 10  $\text{g/ft}^3$  where a 58% conversion efficiency is obtained by the  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat compared with a 47% conversion efficiency for the  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat.

As discussed in the next section, the lower conversion efficiencies experienced by the catalysts containing the ceria additive is due to the detrimental interactions of ceria with the palladium and rhodium metals and the loss of the oxygen-storage capacity for the ceria additive after aging.

### 4.7 Explanation of Aging Effects on Loading and Washcoat

From the results obtained in the present investigation, the thermal deactivation of the catalyst as a function of aging is apparent. The thermal degradation of the catalysts seems most evident in the prolific loss of  $\text{CH}_4$  conversion capabilities as compared with the CO and  $\text{NO}_x$ . This observation was also made by Usmen et al. [11] in an experimental study conducted on fresh and aged natural gas catalysts with palladium loadings using a

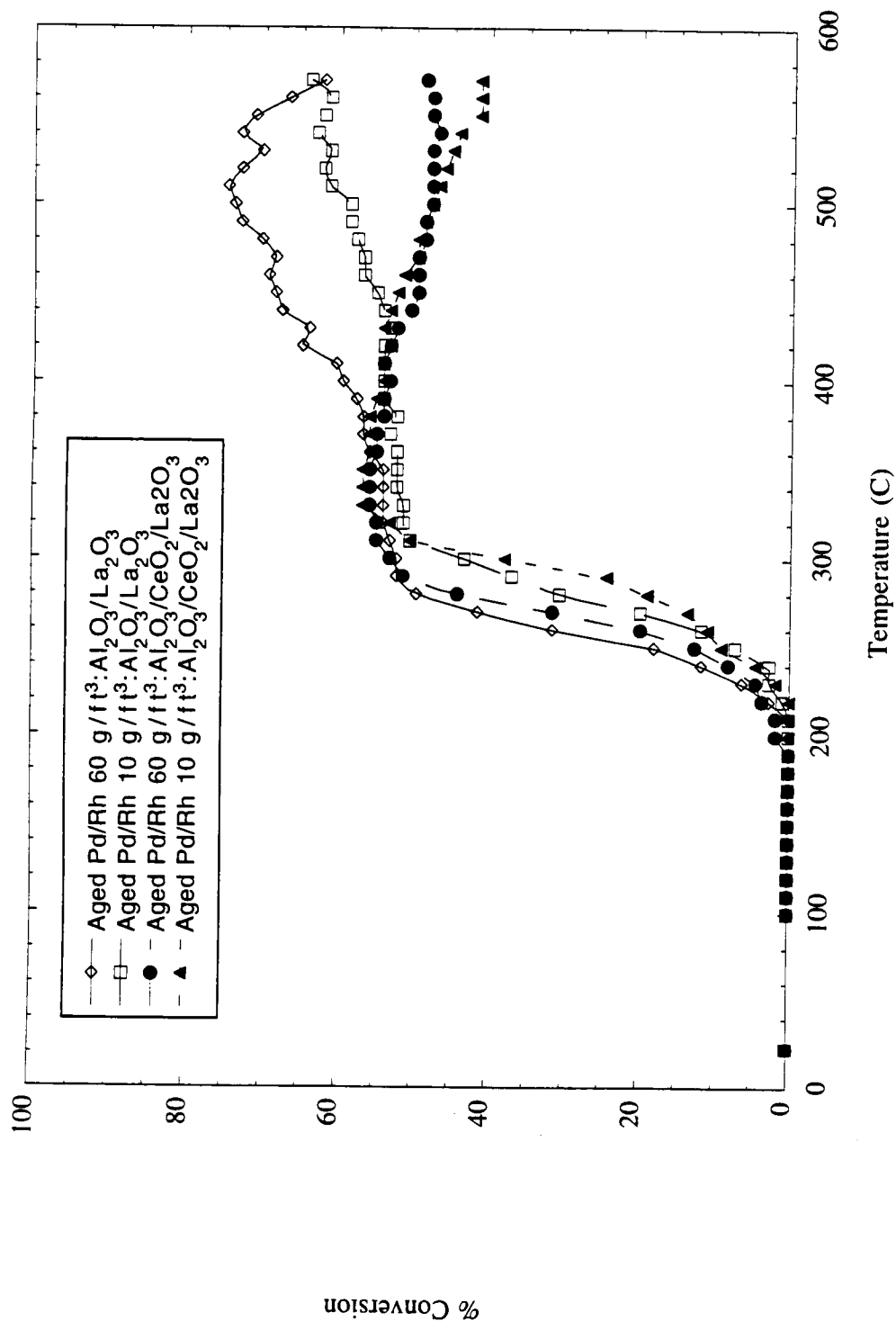


Figure 32: CO Conversion Efficiencies for Aged Catalysts with 10 and 60 g/t<sup>3</sup> Pd/Rh loadings and Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoats in Noncycled Rich Lightoff Tests

bench-flow reactor. Based on their results, they concluded that the reason for the greater amount of methane conversion loss as a result of aging was due to reaction rate limitations. Methane oxidation was more rate limited than CO oxidation or NO reduction; therefore, catalysts sintering effects were more likely to show up in the CH<sub>4</sub> oxidation process.

From the comparison of washcoat performance, the advantage of using the Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat as opposed to the Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat for an aged catalyst is apparent. Some researchers have suggested that the addition of ceria to the washcoat can help catalyst durability. However, for the aging process presented here, the opposite is true. This finding is also supported by Theis, Casarella and Mahan [23]. Their experimental results indicate that at temperatures above 800° C in aged catalysts containing ceria the precious metals and ceria coalesce to form larger particles. As a result, the significant oxygen storage/release as well as much of the other benefits that ceria brings to the catalyst is lost.

The processes leading to thermal deactivation include 1) the loss of active noble metal surface area through sintering, 2) undesirable interactions of the noble metals with the washcoat, 3) the formation of less active noble metal alloys and 4) the loss of the washcoat surface area through sintering or chemical phase change [32].

Thermal deactivation through the loss of active noble metal surface area through sintering occurs in the following manner. As the catalyst reaches elevated temperatures, the noble metals tend to migrate together to form larger particles of palladium and rhodium agglomerations. These agglomerations tend to have less catalytic activity due to their reduced surface area on the catalyst as compared with palladium and rhodium being evenly dispersed on the fresh catalyst surface as illustrated in Figure 33.

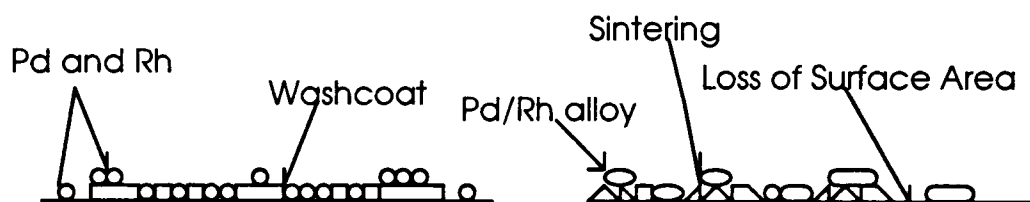


Figure 33: Fresh versus Aged Catalyst Comparison

The migration of noble metals can also lead to the formation of less active noble metal alloys as shown above. This process occurs when the palladium and rhodium metals bond at elevated temperatures. The resulting Pd/Rh alloy has less catalytic activity as compared with palladium and rhodium metals existing on the catalyst surface independently [15, 32]. As discussed in Chapter 2, palladium and rhodium metals have distinct catalytic characteristics when in contact with carbon monoxide, nitrogen oxide and methane. The combination, or alloying, of the metals does not result in combined benefits, but rather a loss of their independent attributes.

Another thermal deactivation process occurring in the catalyst is the undesirable interactions between the noble metals and the washcoats, and the loss of washcoat surface area through sintering. One of the main causes for surface degradation is the loss of surface area of alumina [15]. In other words, the loss of alumina surface area accelerates the coalescence of noble metal particles to deteriorate the catalytic performance. The loss of this washcoat surface area forces the palladium and rhodium metals into closer proximity which leads to the alloying of the metals as described previously. Further problems result with the addition of ceria to the washcoat as can be seen from the data generated. At elevated temperatures, the characteristic advantages of ceria are lost and the thermal degradation of the catalyst occurs much more rapidly in the presence of ceria and the reduced presence of alumina.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

The results of this research demonstrate the effects of feed stream composition, precious metal loading and washcoat composition on the conversion efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO in natural gas catalysis. In addition, the thermal degradation of the aged catalysts as a function of these parameters is shown to greatly influence the effectiveness of the catalysts in reducing the presence of these constituents in the feed stream. The optimum feed stream composition for maximized conversion efficiencies of these constituents is shown to occur in a cycled stoichiometric feed stream. This is due primarily to the availability of oxygen during the cyclic variation of the feed stream composition which leads to enhancing both the reduction and oxidation of the constituents.

The conversion of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO is found to be maximized with higher palladium and rhodium loadings for both the fresh and aged catalysts. However, the fresh catalyst with a Pd/Rh loading of  $60 \text{ g/ft}^3$  did not offer a significant conversion efficiency advantage over the fresh catalyst with a loading of  $40 \text{ g/ft}^3$ . Hence, it can be concluded that the configurations of the fresh catalysts investigated are optimized at a Pd/Rh loading of  $40 \text{ g/ft}^3$ . As mentioned previously, the price and availability of these precious metals is a serious concern for catalyst designers, therefore the implications of achieving compatible conversion results with lower Pd/Rh loadings is a significant result of this research.

For the aged catalysts studied, the degree of thermal degradation of the catalysts is shown to be a function of the amount of precious metal loading on the catalyst, especially in the conversion of methane. Therefore, the future requirement for automobile catalysts

to reduce vehicle emissions to within federal standards over 100,000 miles may require higher amounts of precious metals to achieve the higher levels of catalyst durability.

The effects of ceria additions to the alumina/lanthana washcoat was found to enhance the conversion efficiencies of nitrogen oxides and carbon monoxide due to its characteristic oxygen storage capacity. However, the ceria addition did not offer higher conversion results for methane in lean, rich and stoichiometric feed stream simulations. In addition, it was found that the ceria addition resulted in a higher degree of thermal degradation than the ceria-free catalysts after aging, particularly with respect to methane conversion. Therefore, the results of this investigation lead to the conclusion that ceria additions do give higher conversion results for fresh catalysts, but not after high temperature aging. Consequently, for the conditions that will be encountered in commercial applications such as NGV engines, the ceria additions to these catalyst configurations would prove to significantly decrease the durability and performance of the catalyst over time.

It is recommended that further investigations be conducted using dynamometer tests employing a dedicated NGV engine with the catalyst configurations used in this study. The dynamometer tests can be used to substantiate the findings in regards to catalyst precious metal loadings and washcoat compositions revealed in this study. The superior performance of ceria in the reduction and oxidation of CO and NO<sub>x</sub> for the fresh catalysts but not for the aged catalysts should be investigated further. One approach could be to optimize the amount of ceria in the washcoat by varying the level of ceria applied to the catalyst. The optimum level of ceria could then be used to achieve an effective oxygen storage capacity for the catalyst but at the same time resist the effects of thermal degradation. This would in turn lead to a catalyst capable of meeting the federal guidelines for performance and durability in conversions of CH<sub>4</sub>, NO<sub>x</sub> and CO in the exhaust stream.

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## APPENDIX

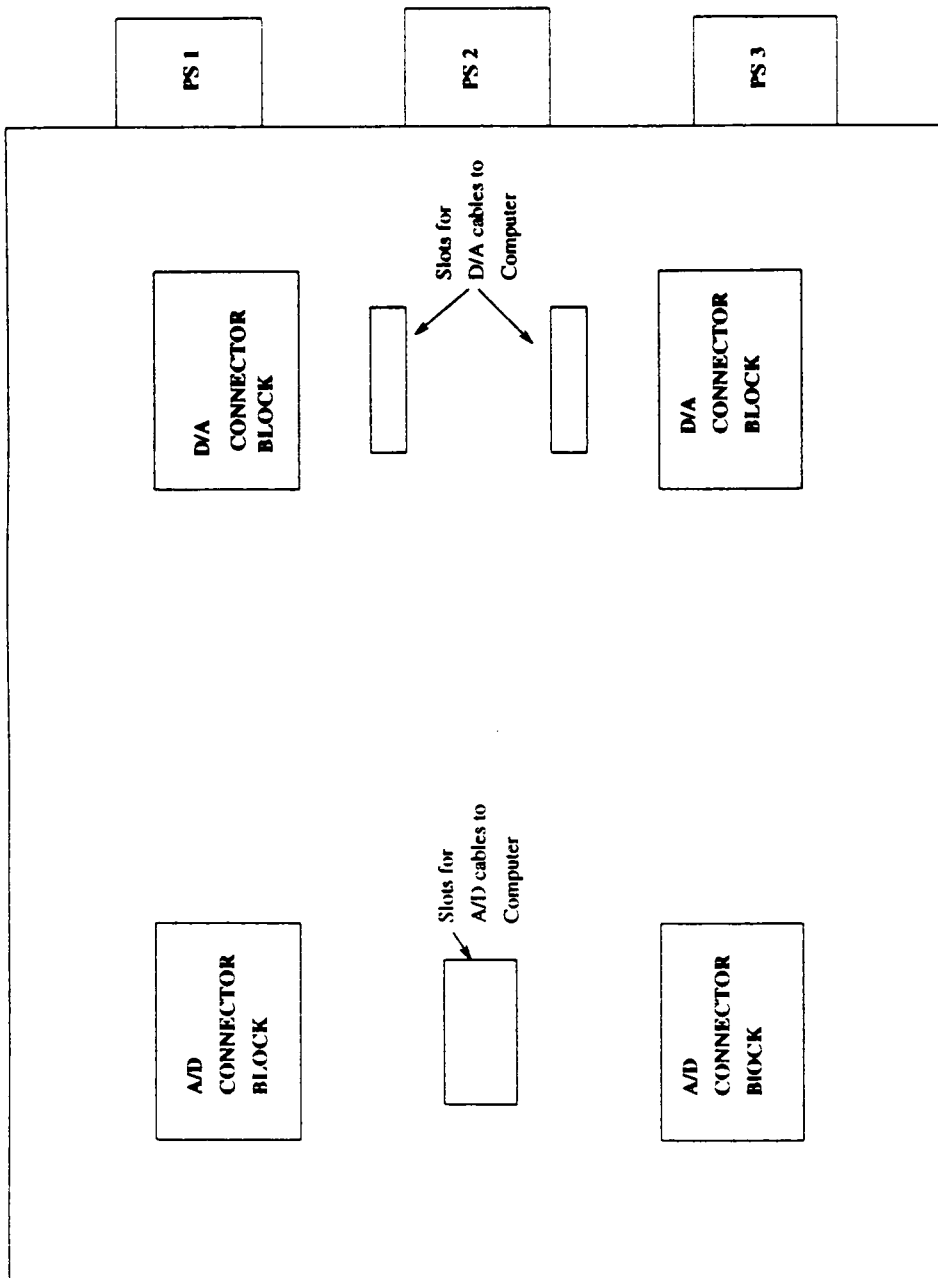


Figure A-1: Top View of Control Board

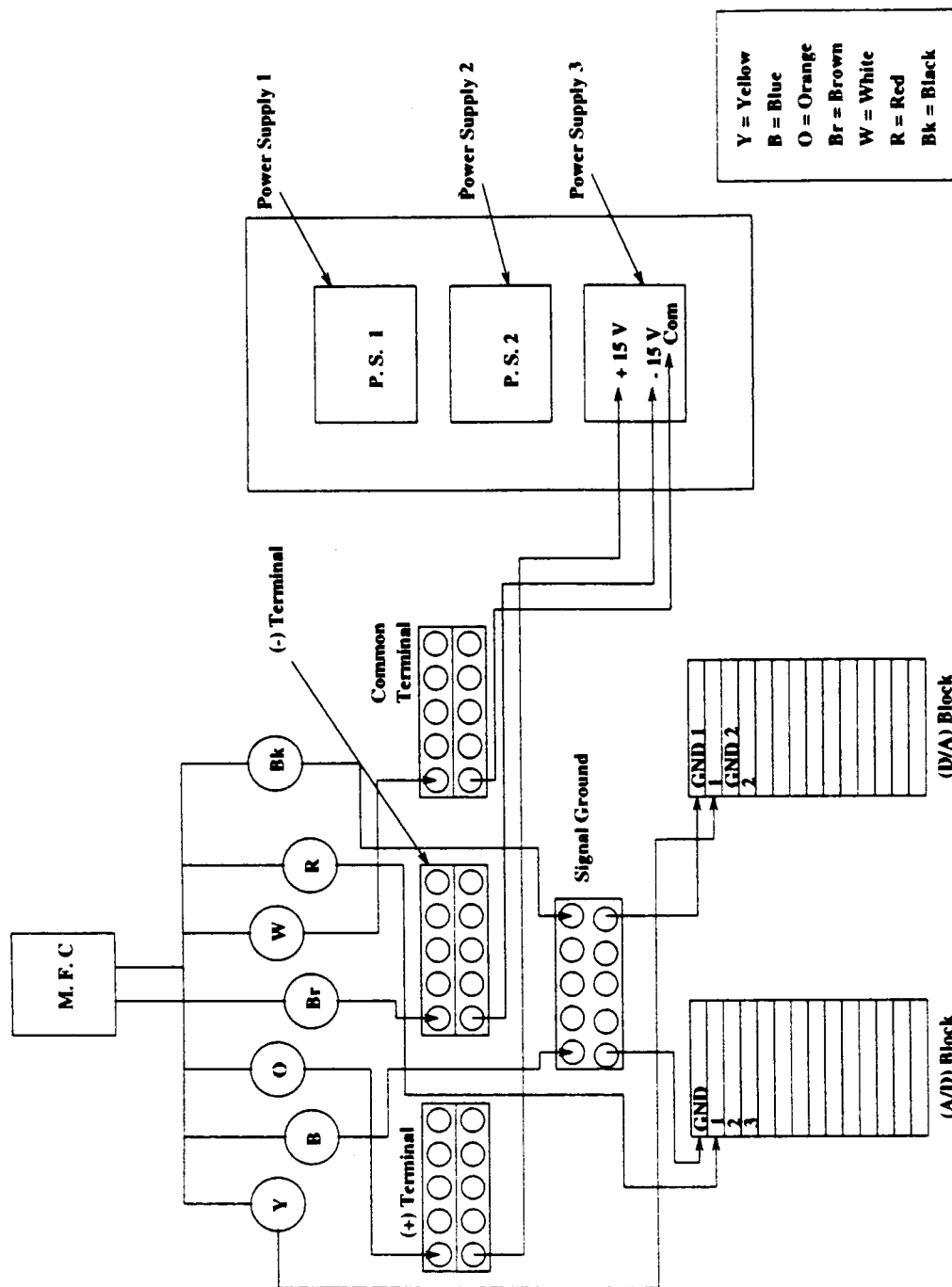


Figure A-2:Electrical Connections of a Typical Mass Flow Controller

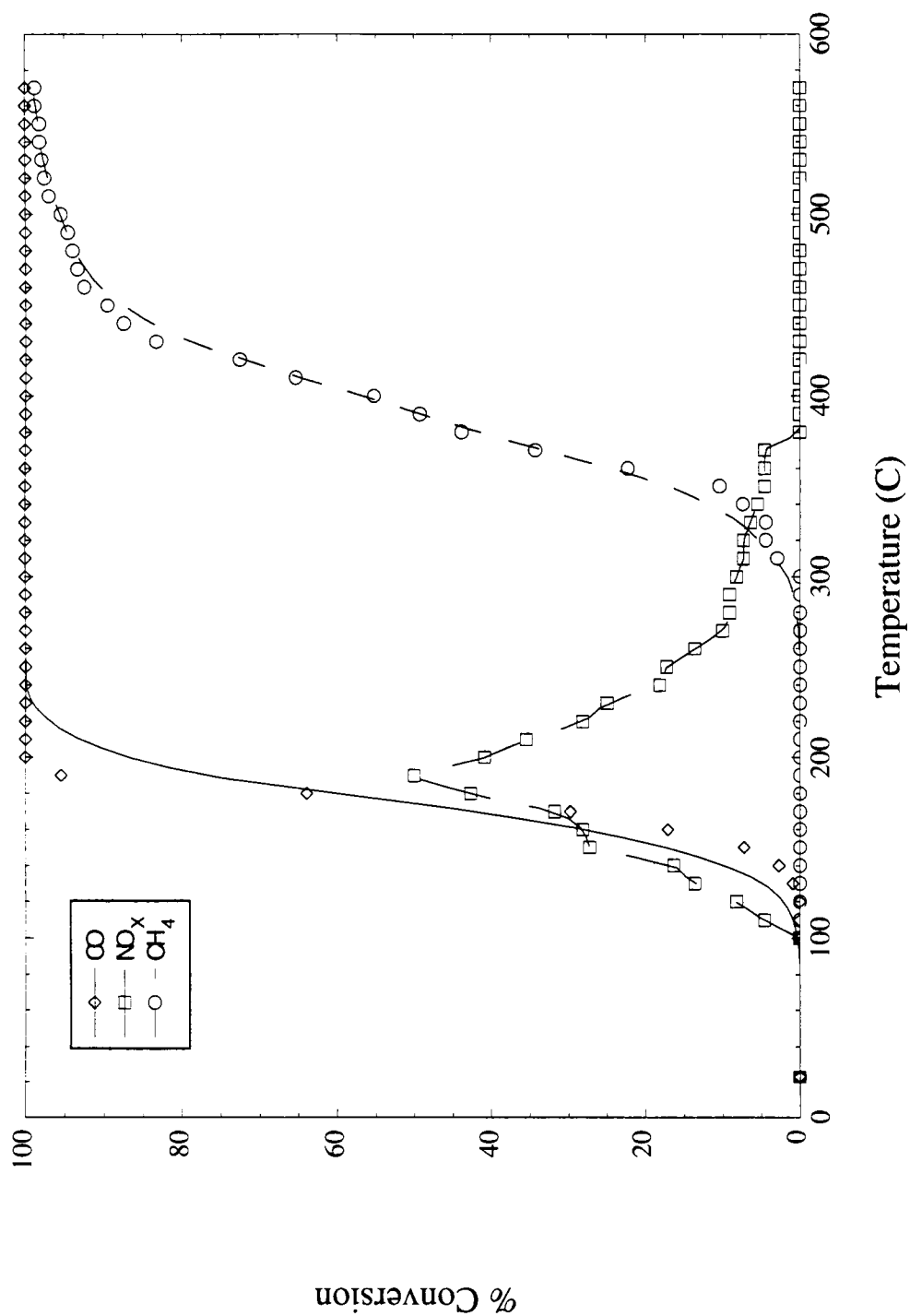


Figure A-3: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for a Fresh Catalyst with a  $60 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Lean Noncycled Lightoff Test

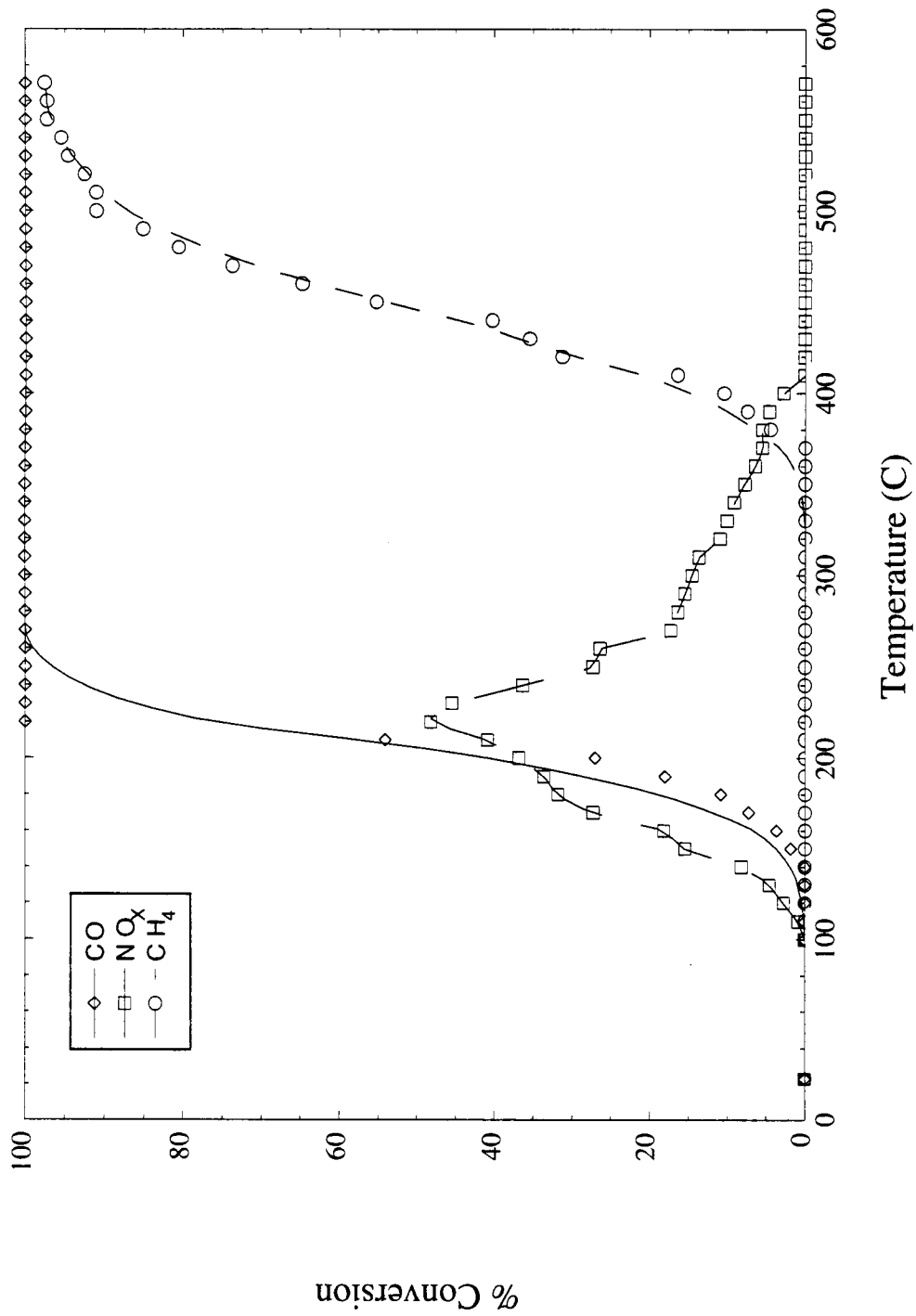


Figure A-4: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

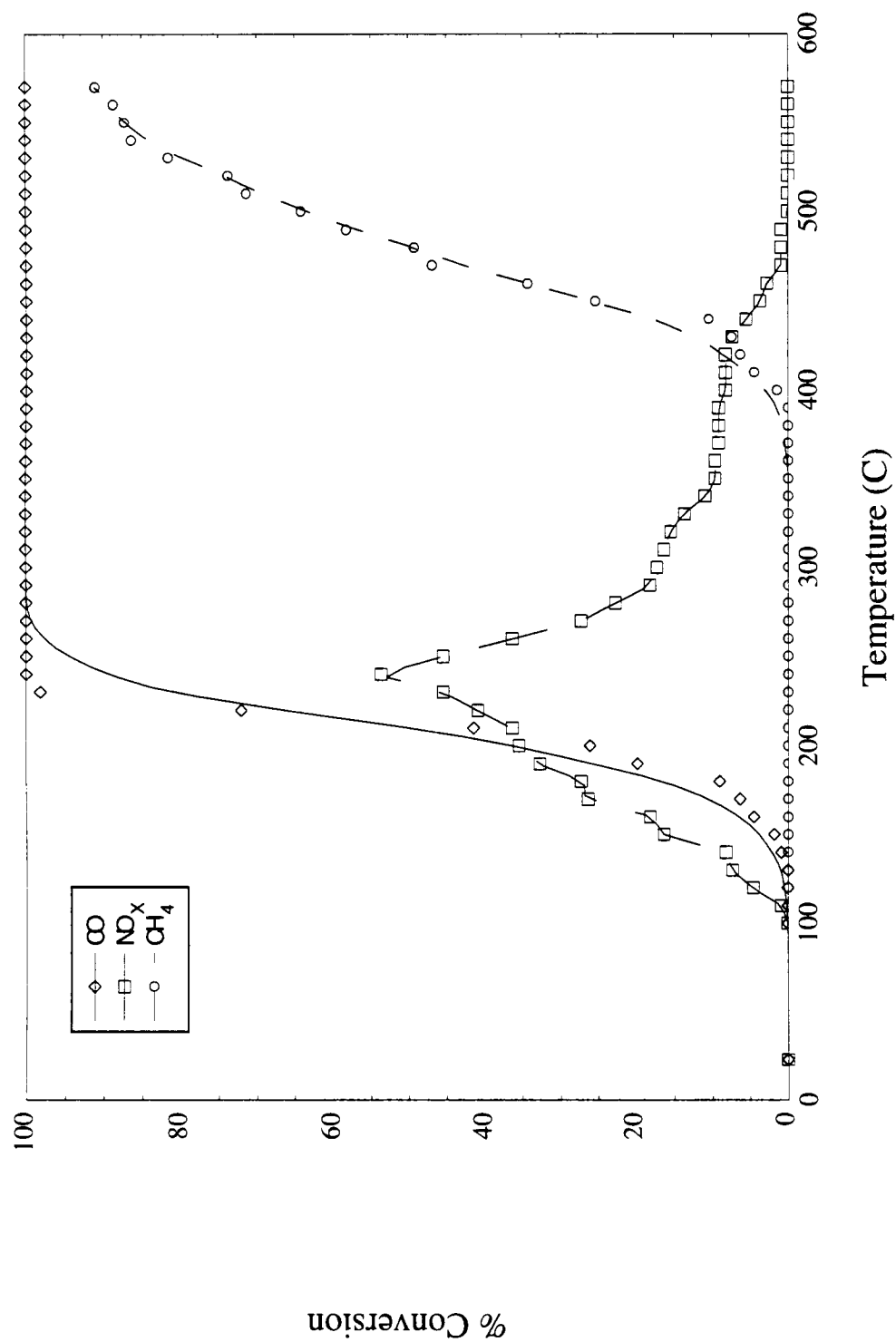


Figure A-5: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for a Fresh Catalyst with a  $10 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Lean Noncycled Lightoff Test

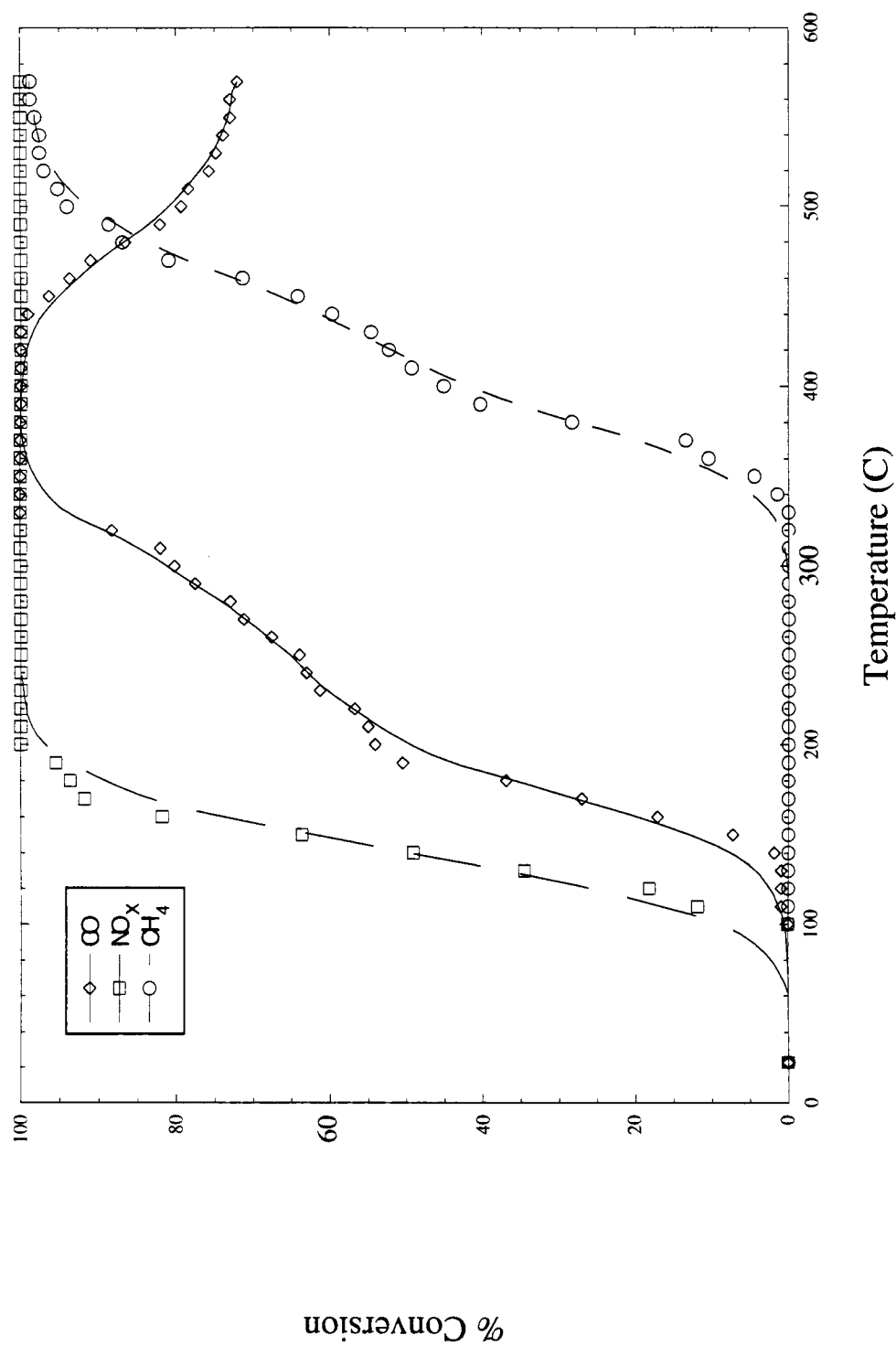


Figure A-6: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Rich Noncycled Lightoff Test

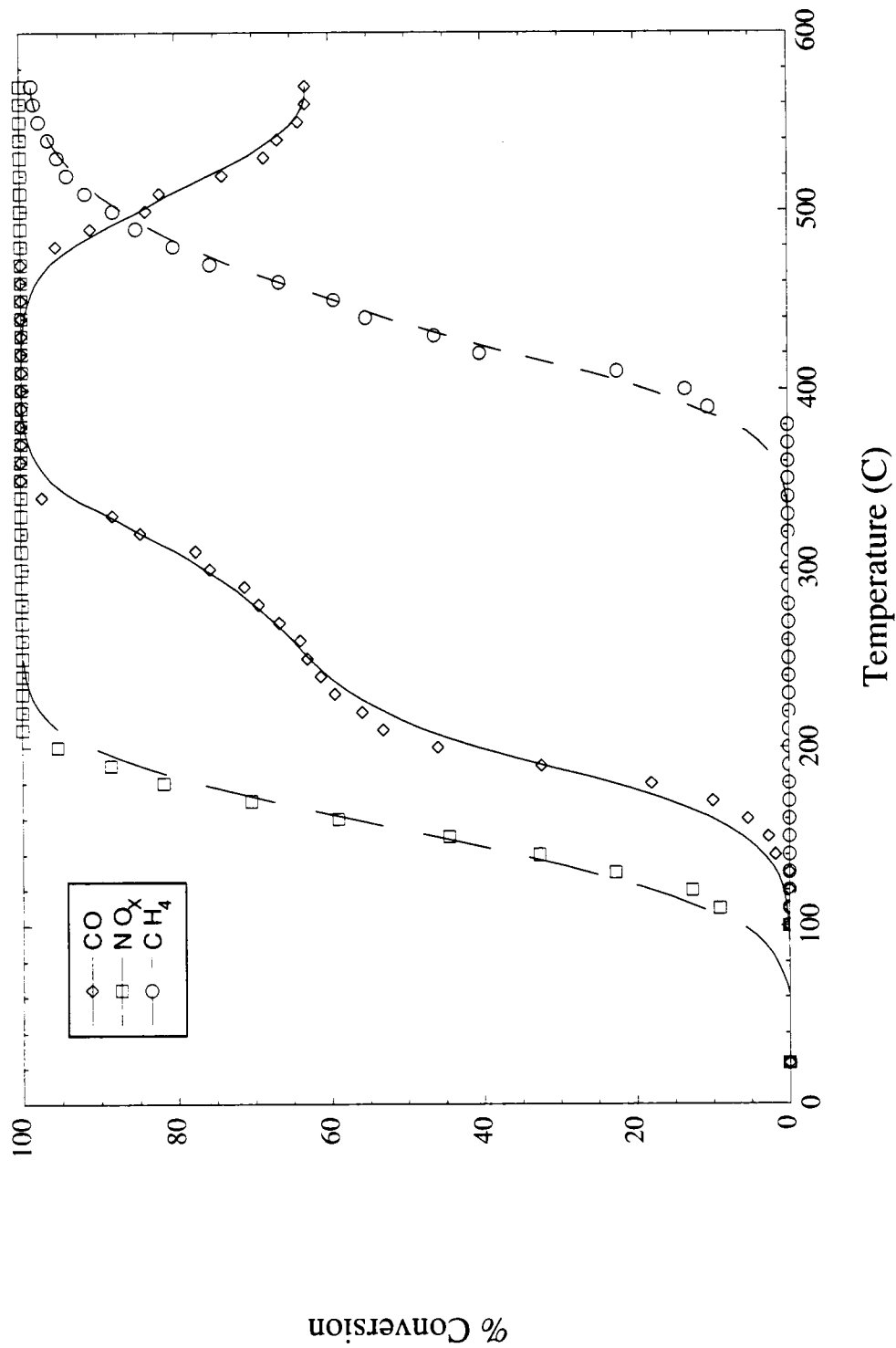


Figure A-7: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Rich Noncycled Lightoff Test

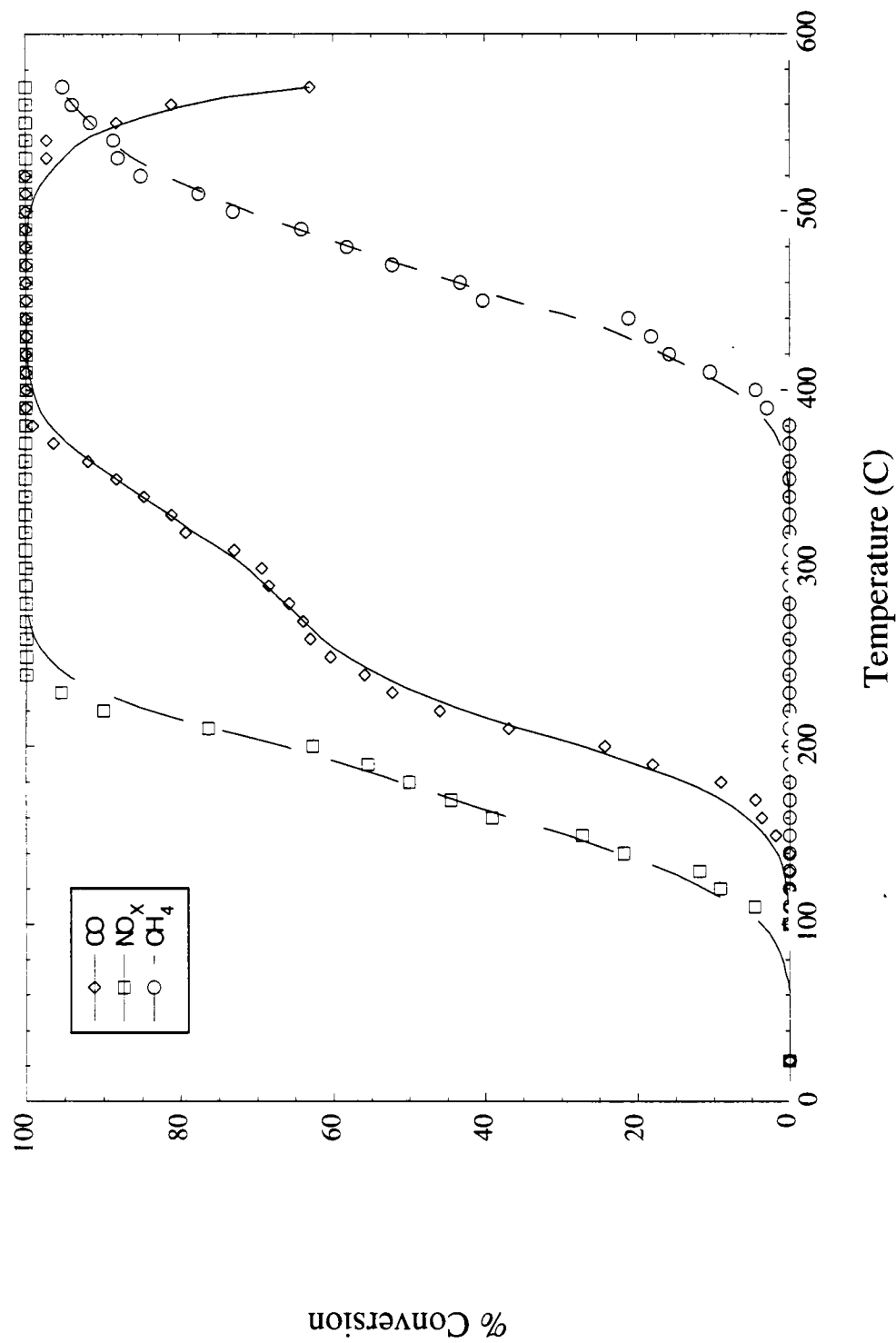


Figure A-8: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for a Fresh Catalyst with a  $10 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Rich Noncycled Lightoff Test

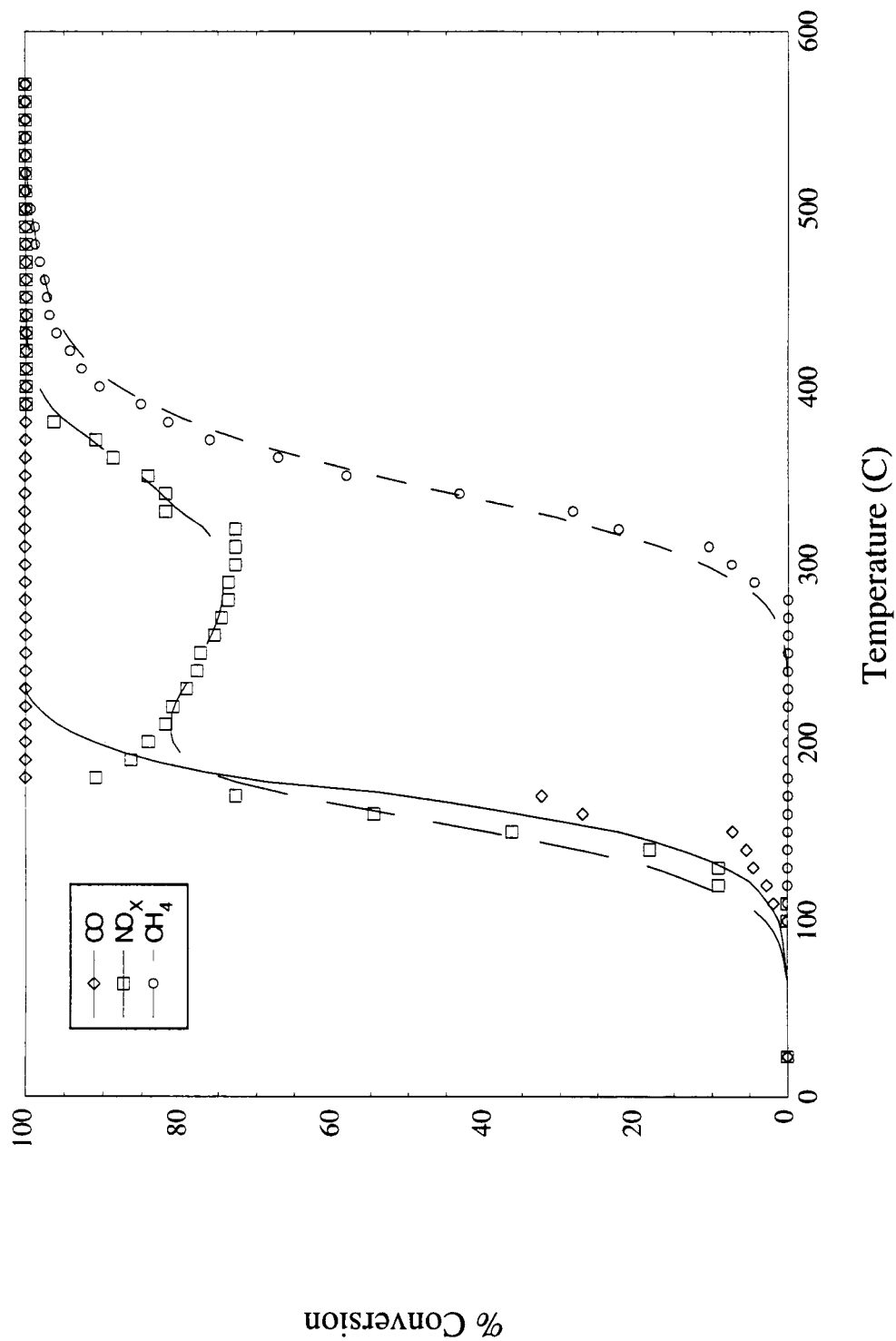


Figure A-9: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for a Fresh Catalyst with a  $60 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Stoichiometric Cycled Lightoff Test

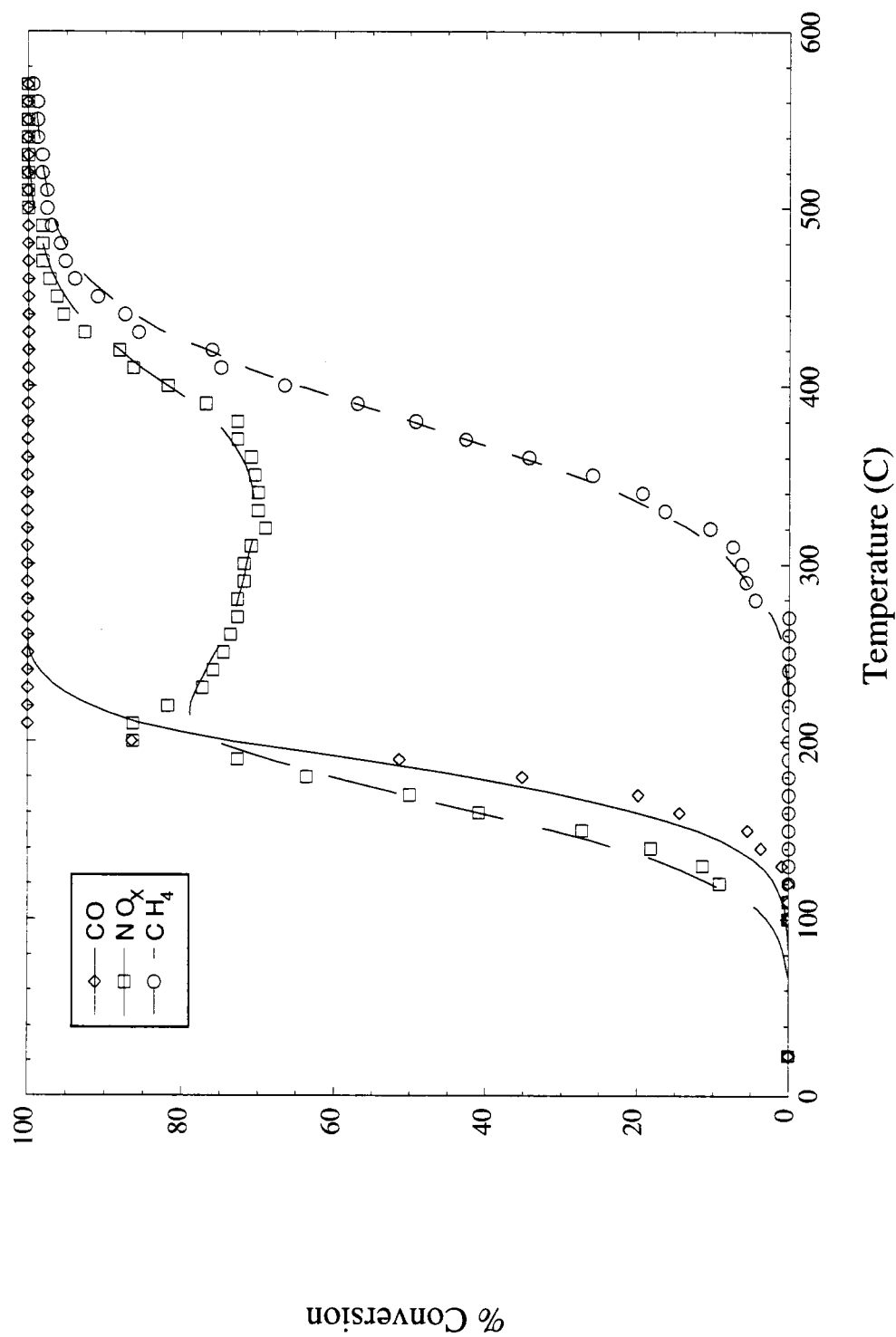


Figure A-10: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoichiometric Cycled Lightoff Test

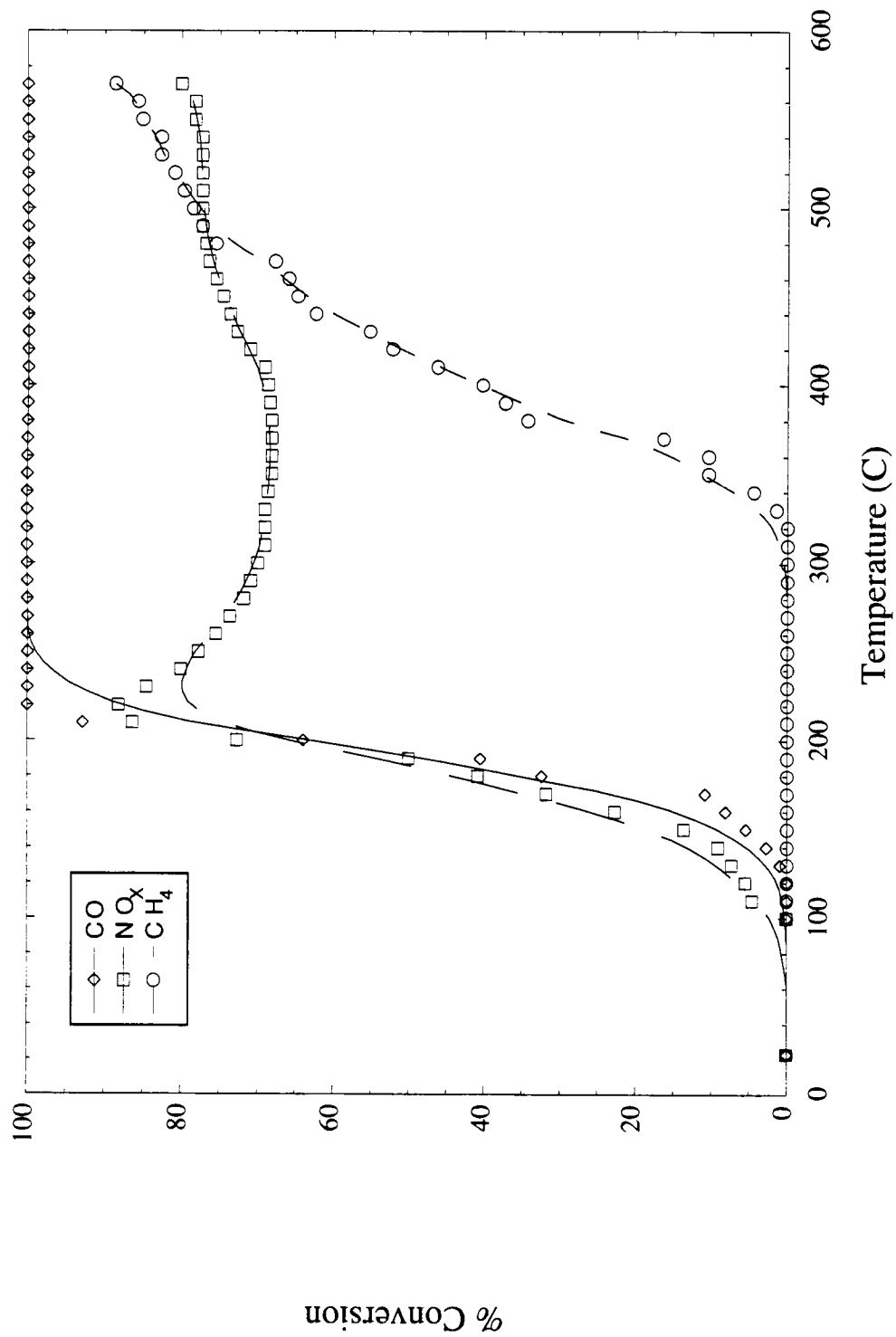


Figure A-11: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

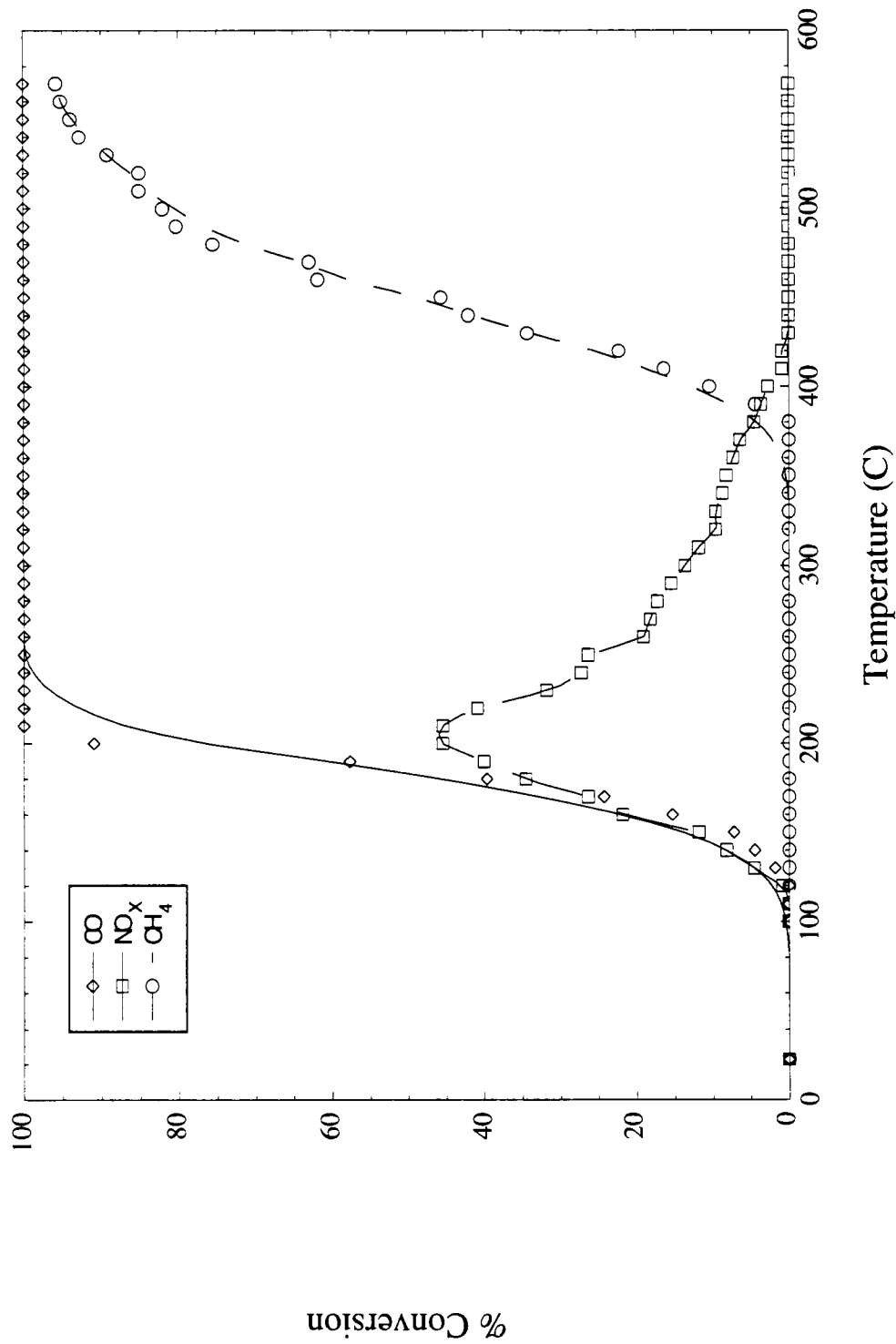


Figure A-12: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

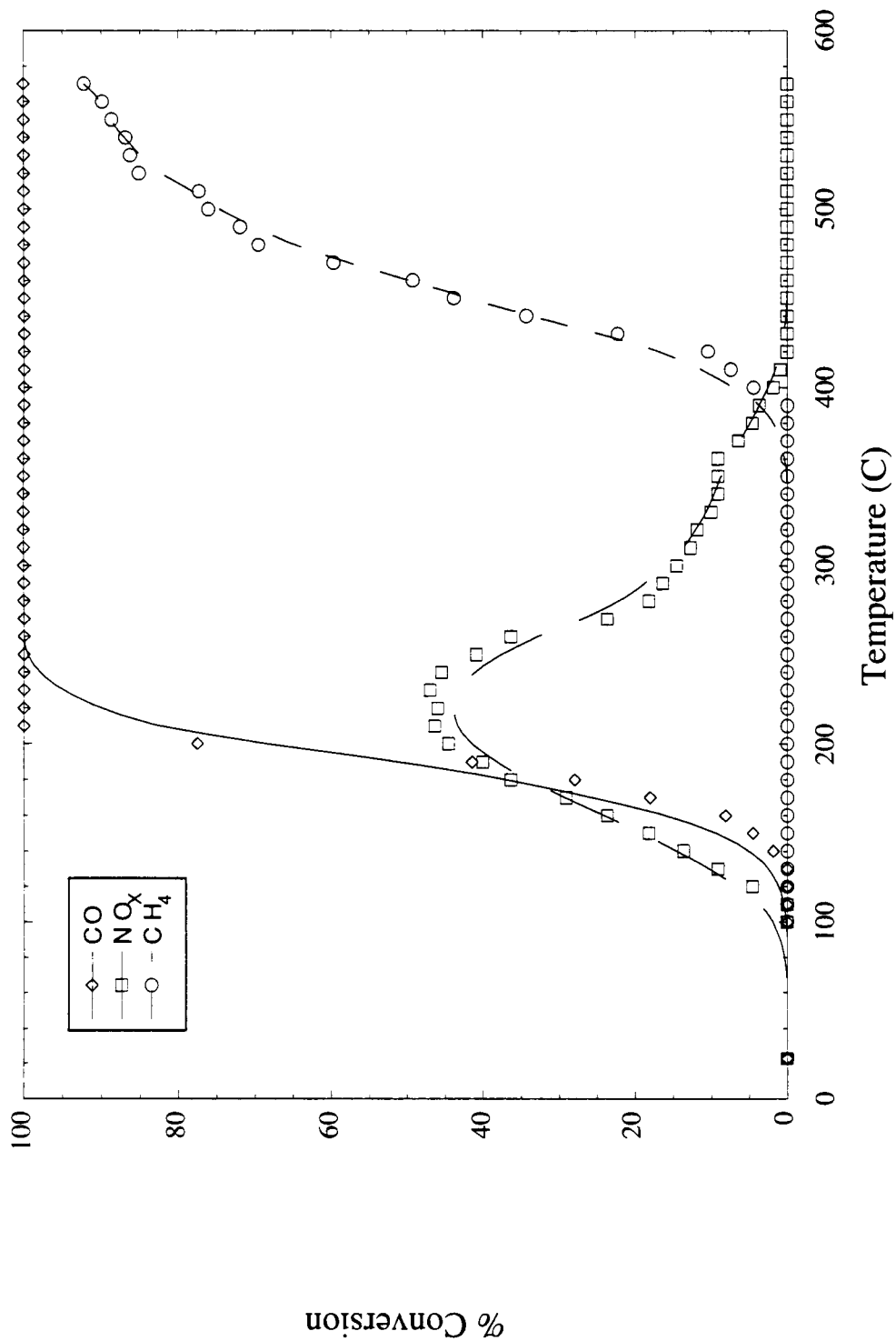


Figure A-13: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

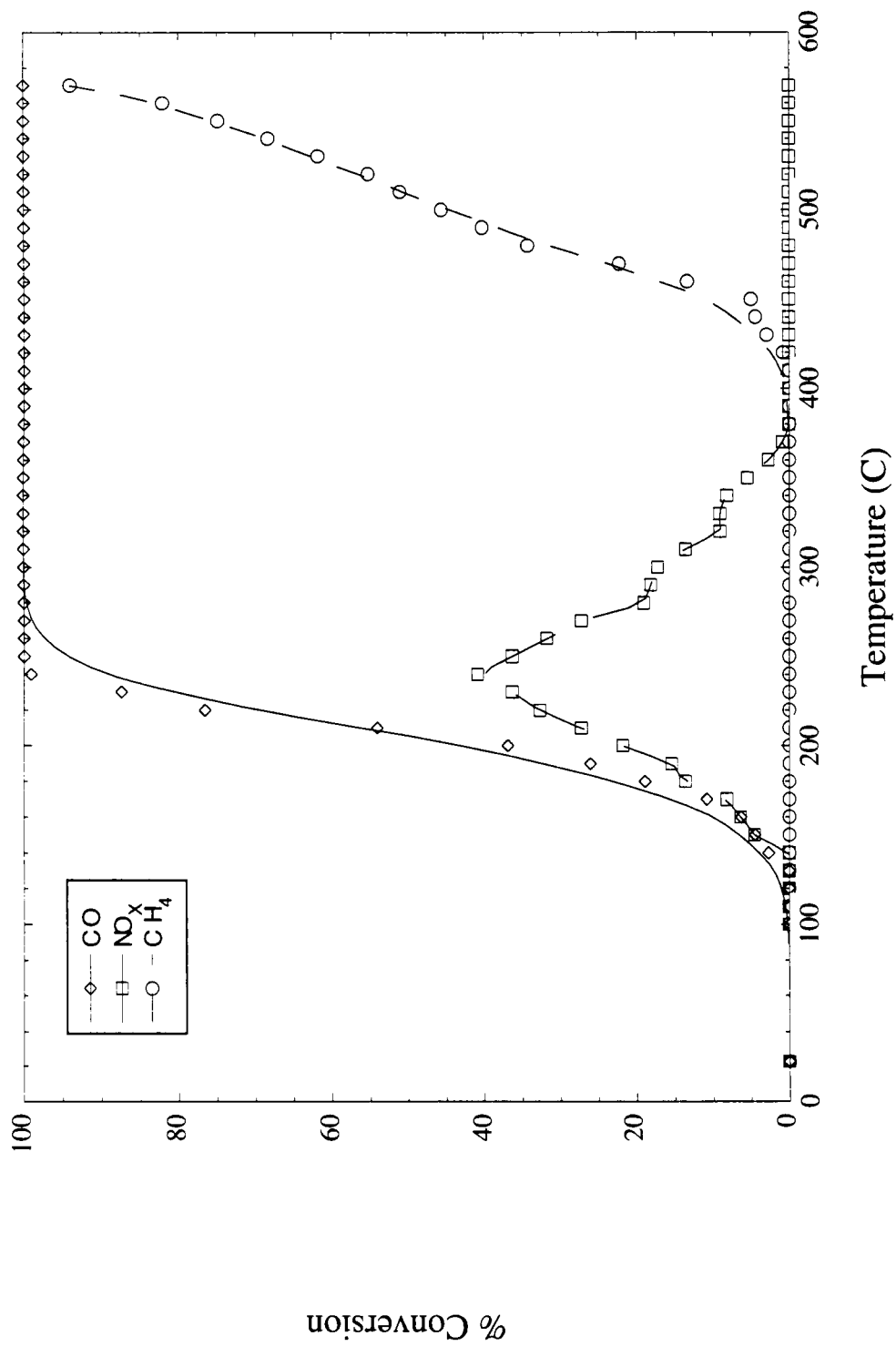


Figure A-14: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

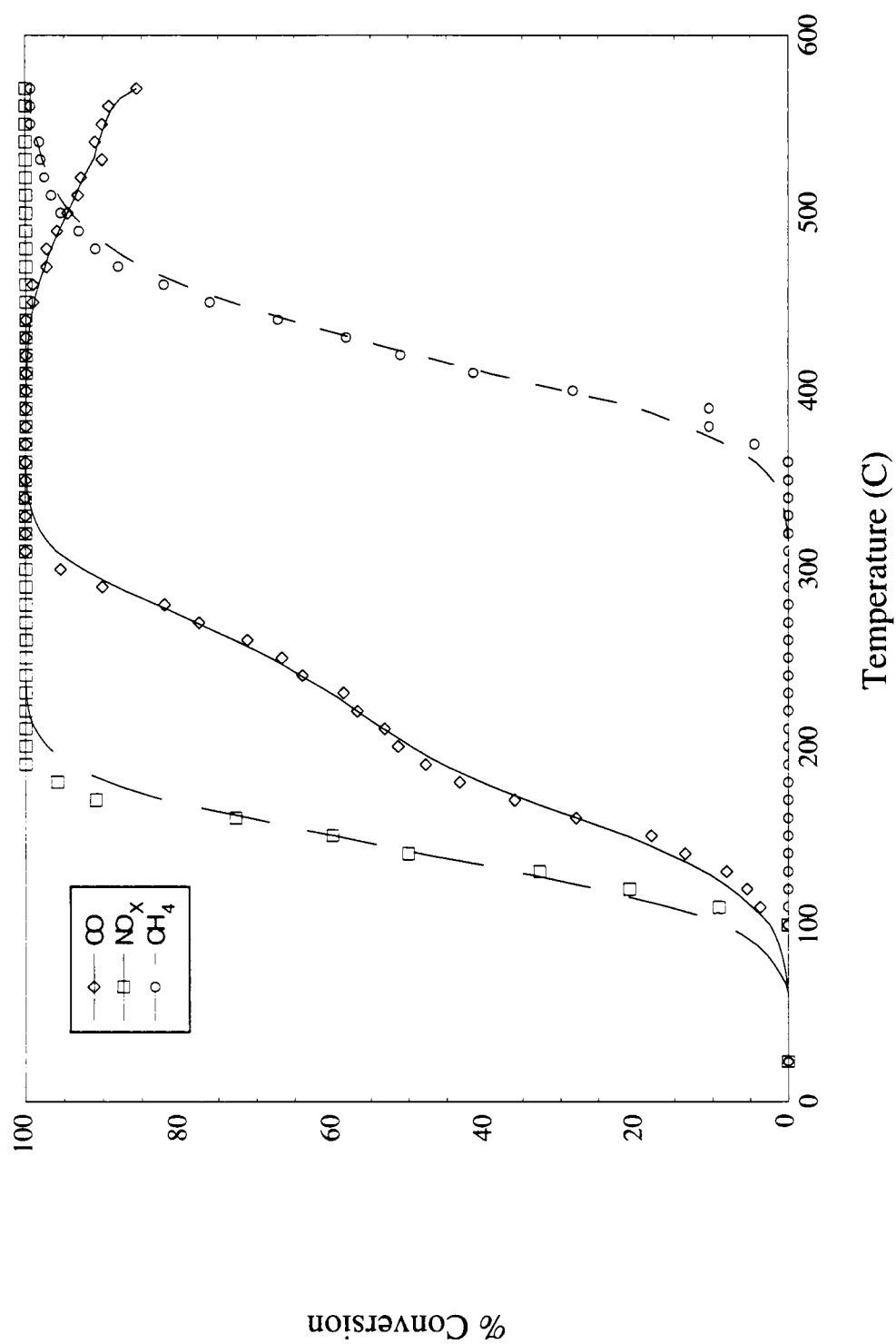


Figure A-15: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Rich Noncycled Lightoff Test

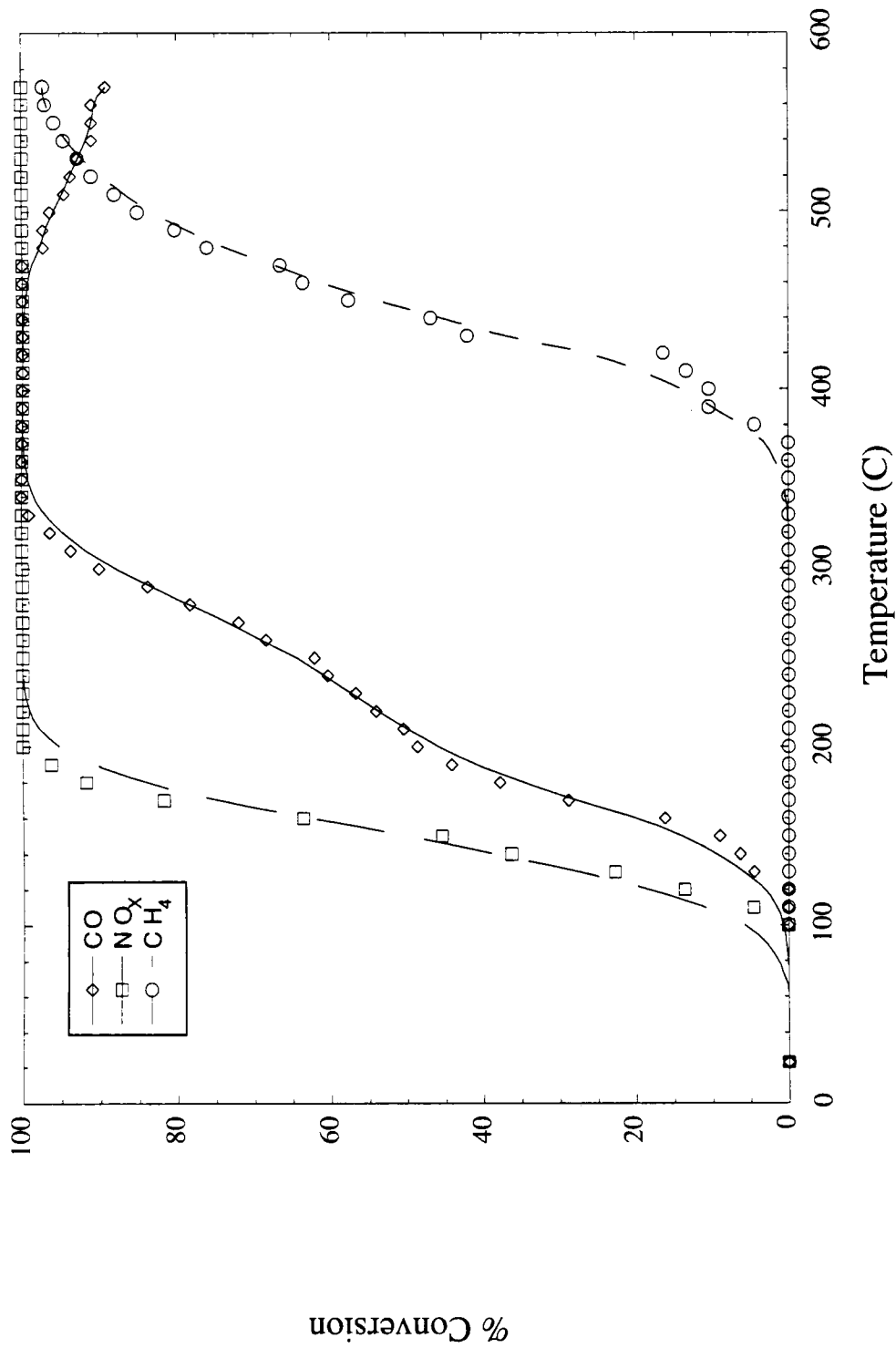


Figure A-16: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Rich Noncycled Lightoff Test

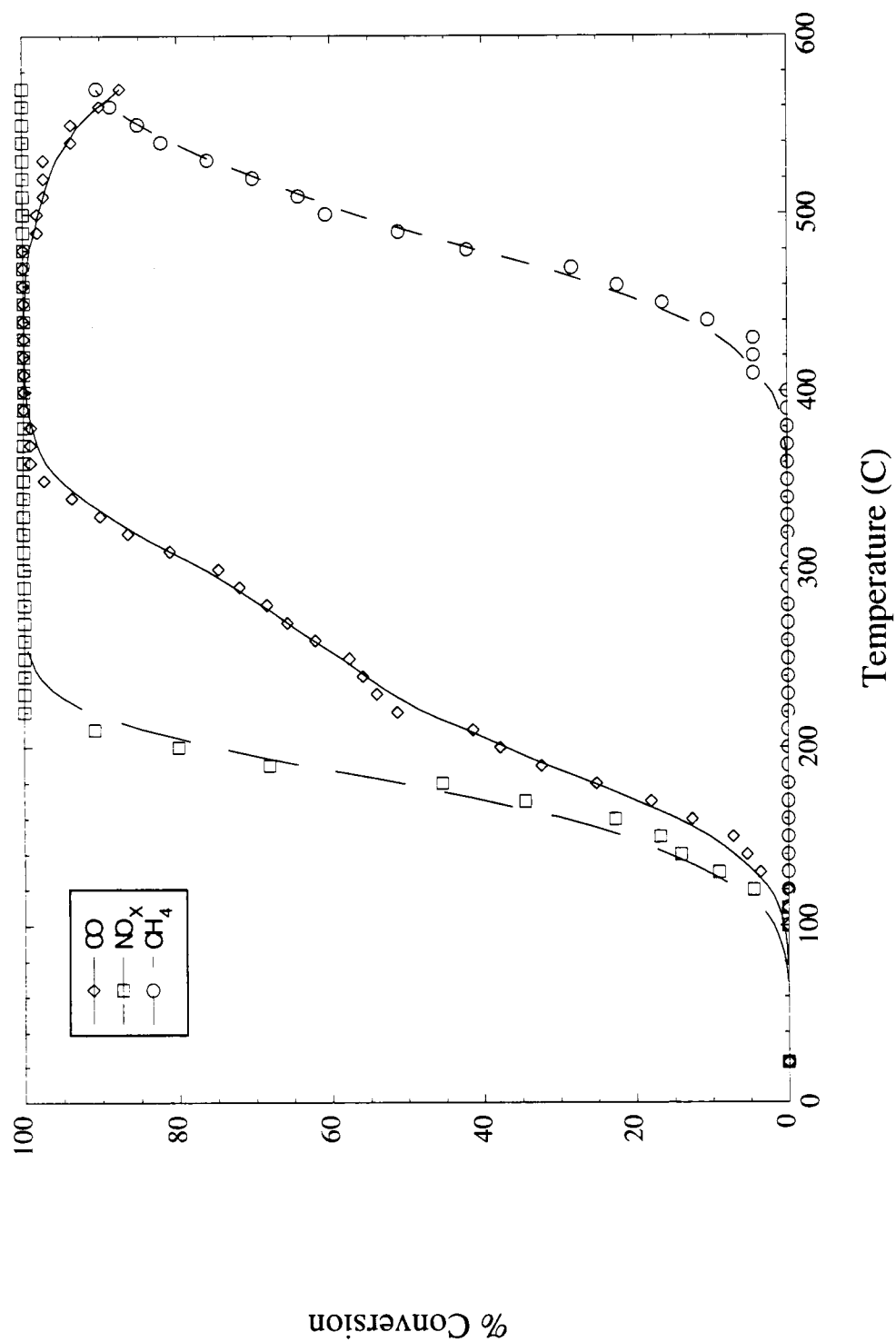


Figure A-17: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for a Fresh Catalyst with a  $10 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a Rich Noncycled Lightoff Test

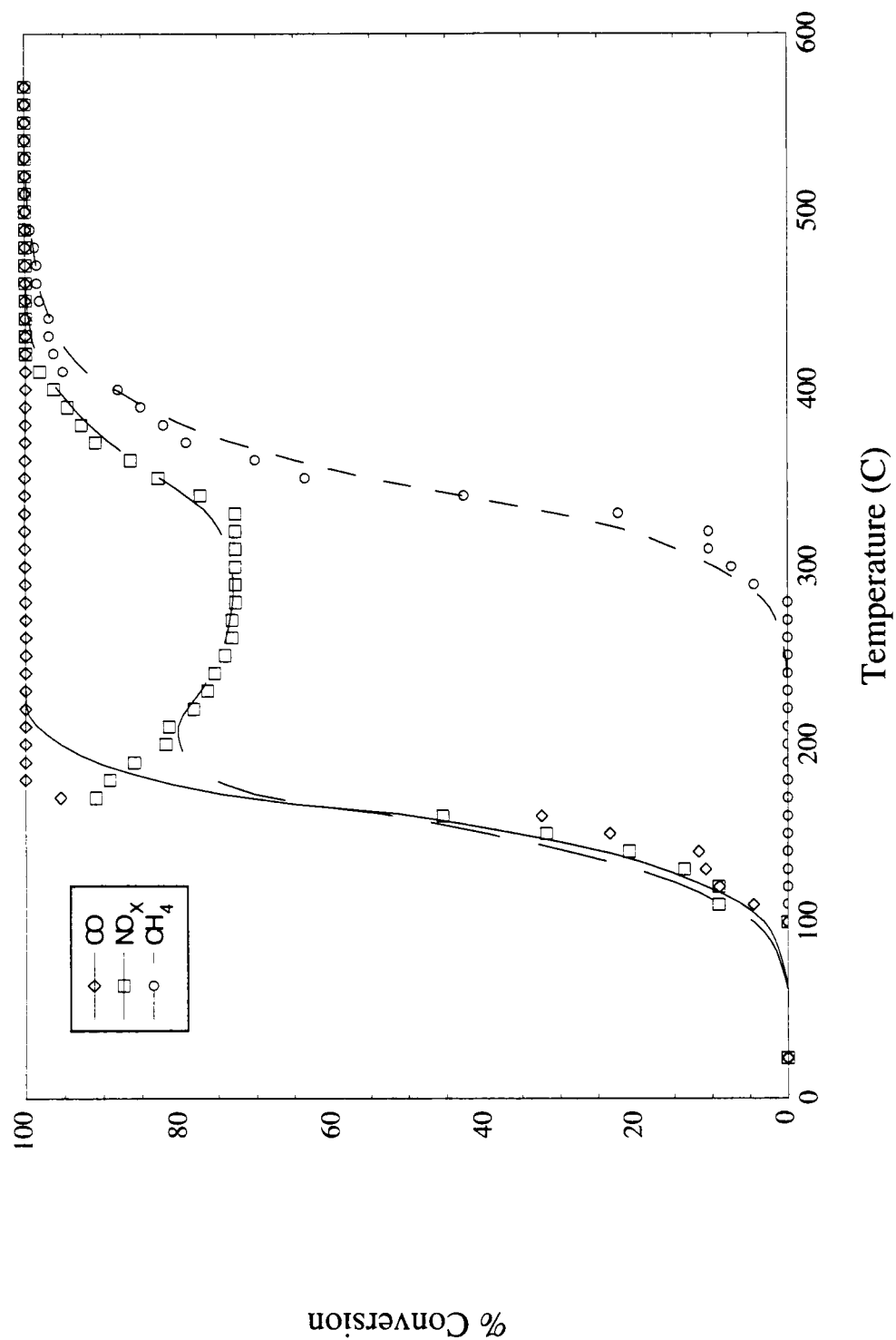


Figure A-18: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

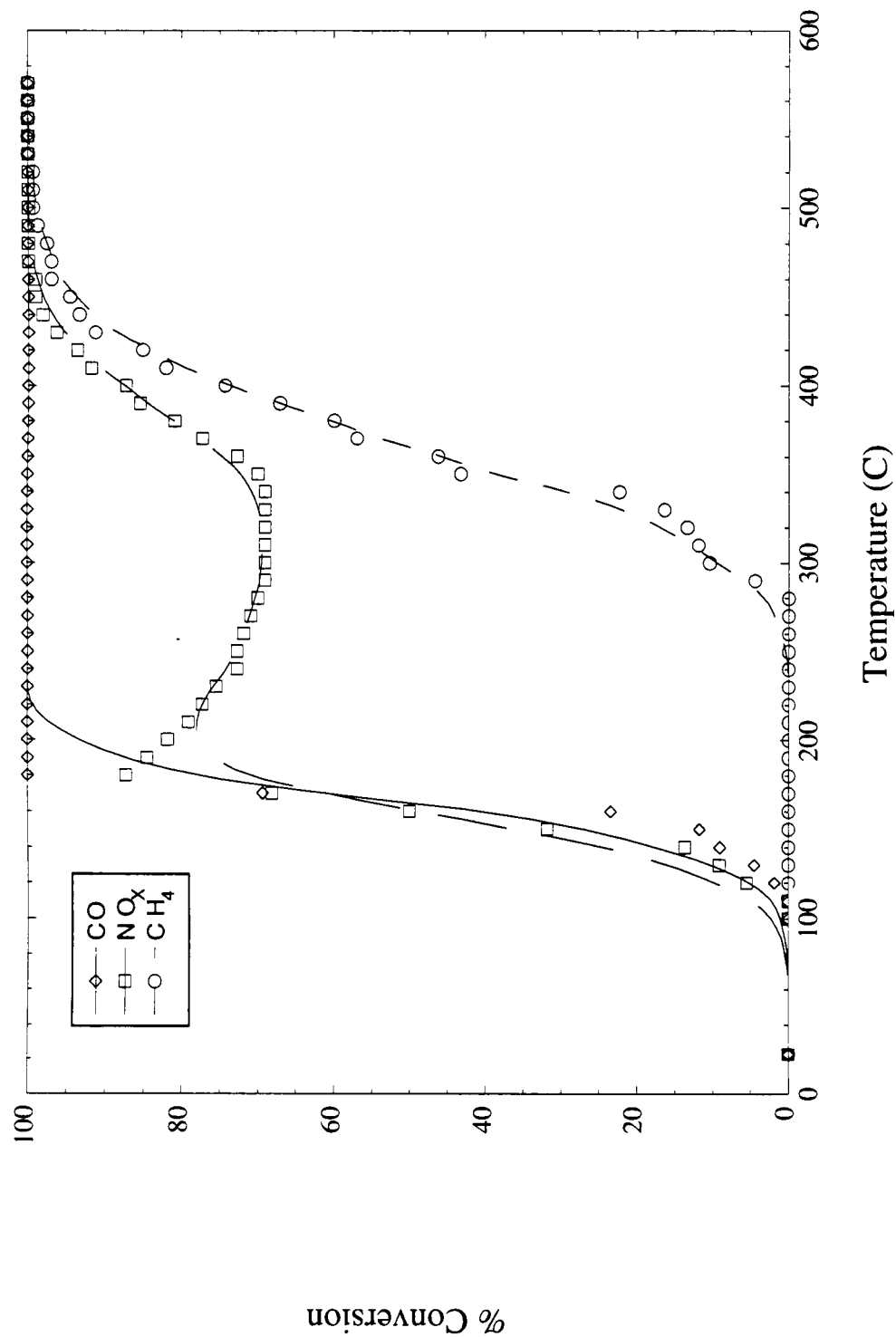


Figure A-19: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 40 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

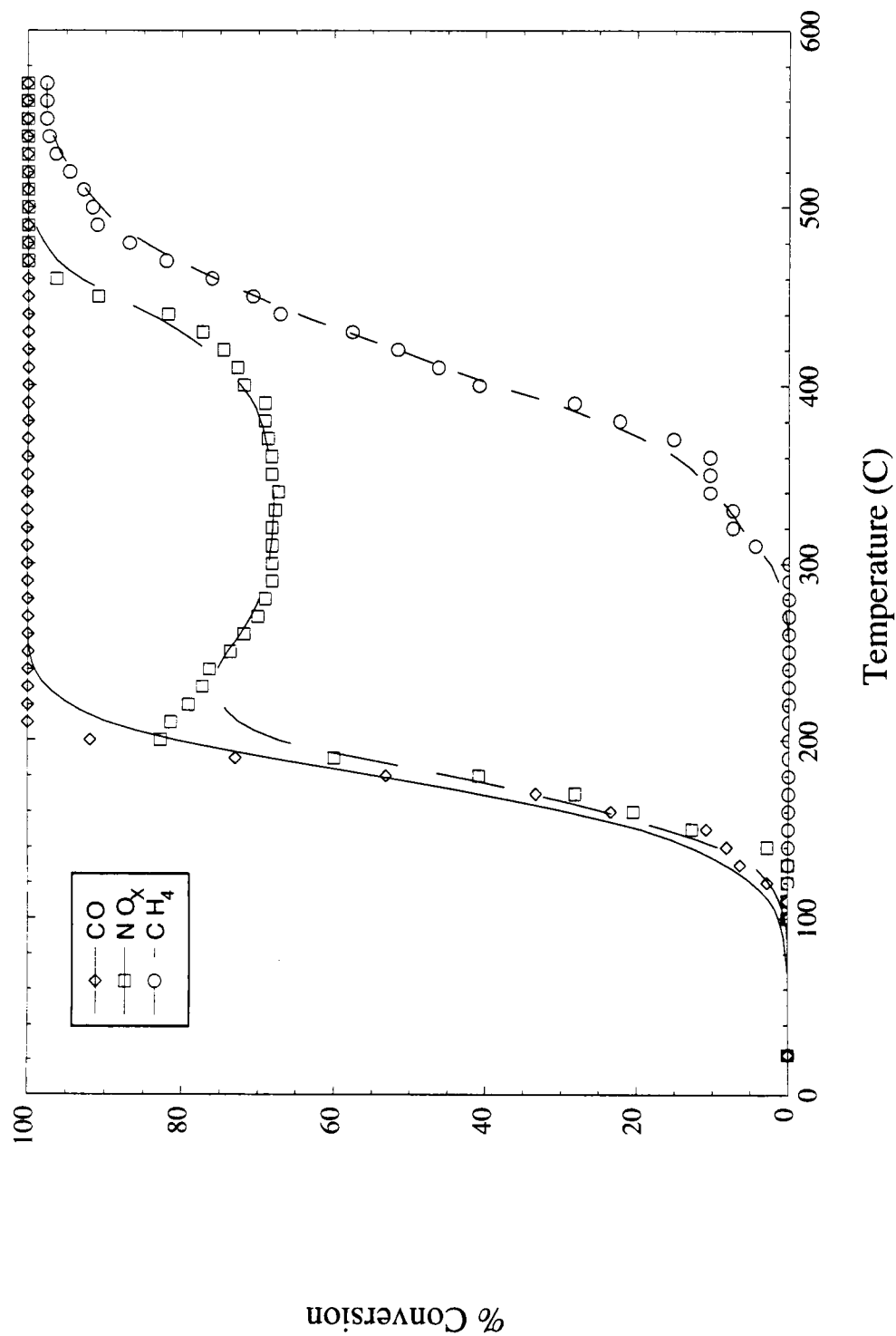


Figure A-20: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Fresh Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

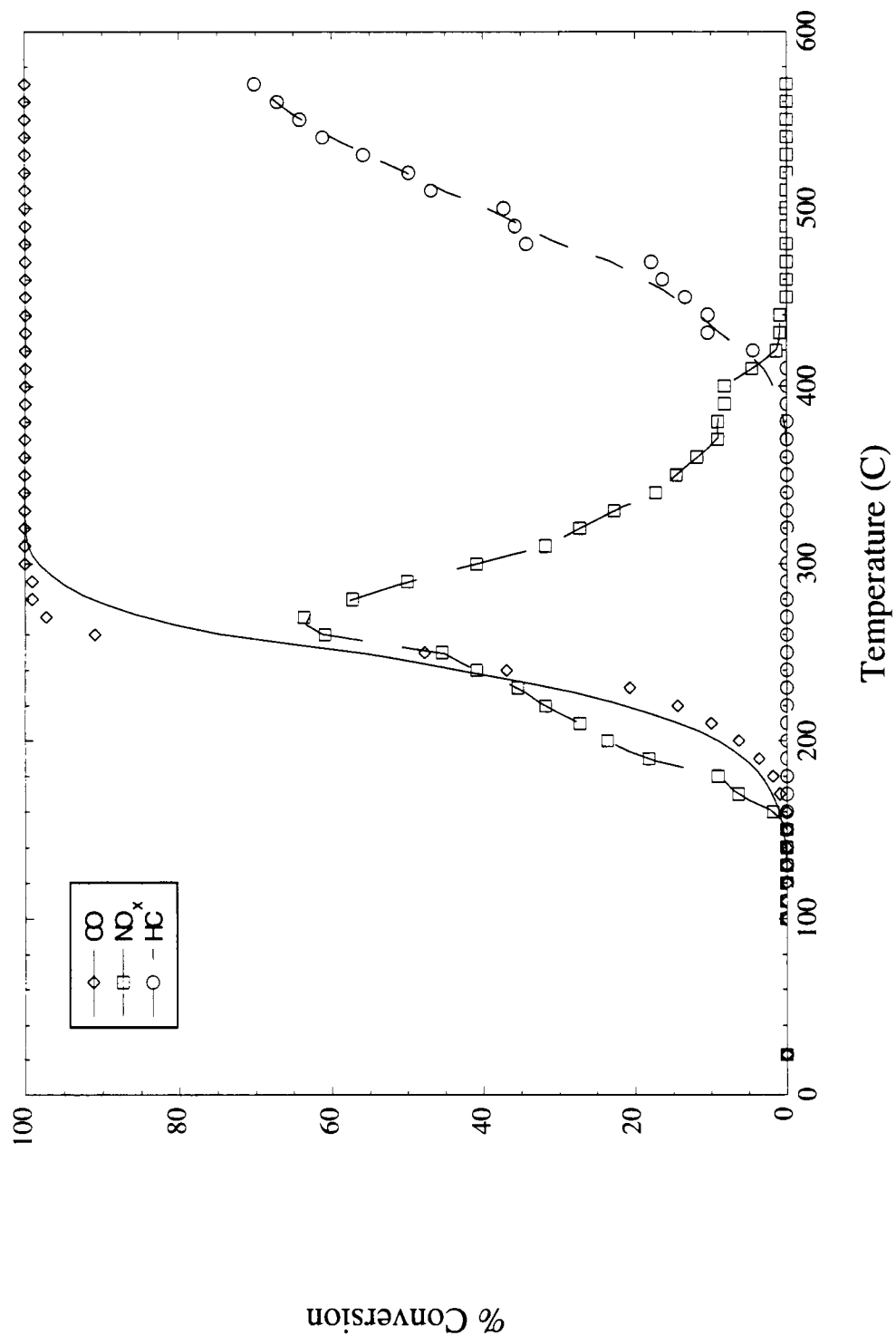


Figure A-21: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

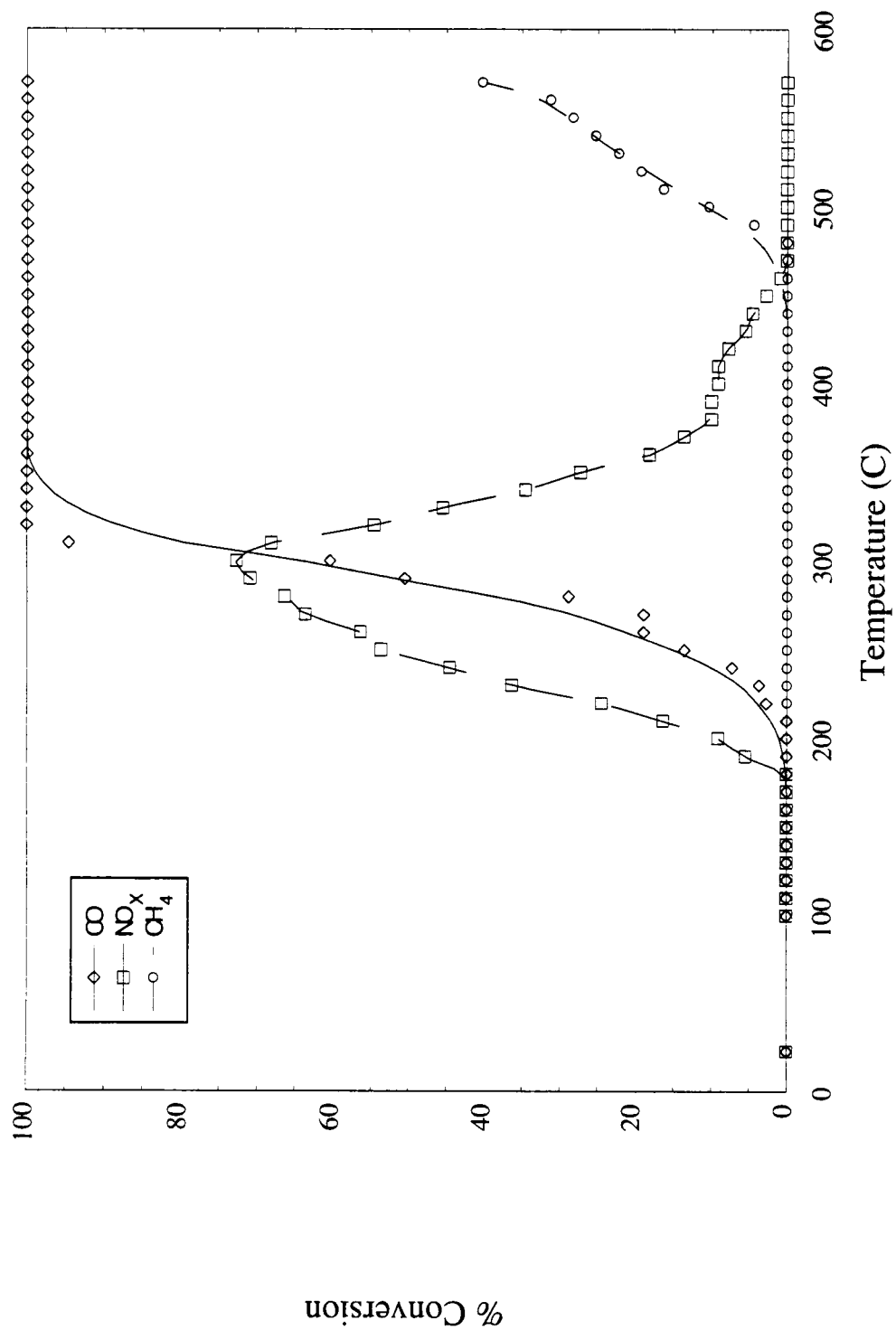


Figure A-22: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for a Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

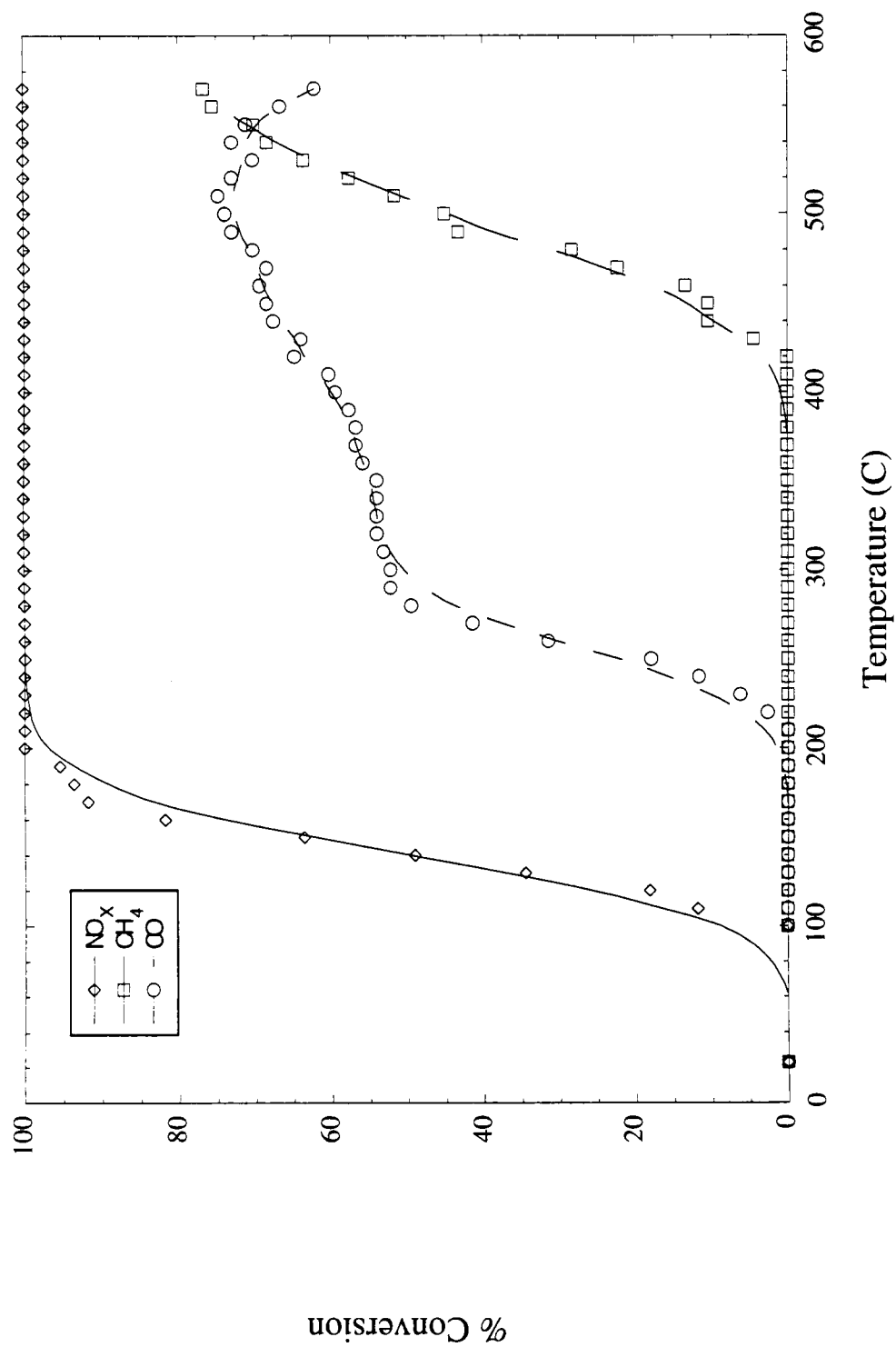


Figure A-23: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO for an Aged Catalyst with a  $60 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Rich Noncycled Lightoff Test

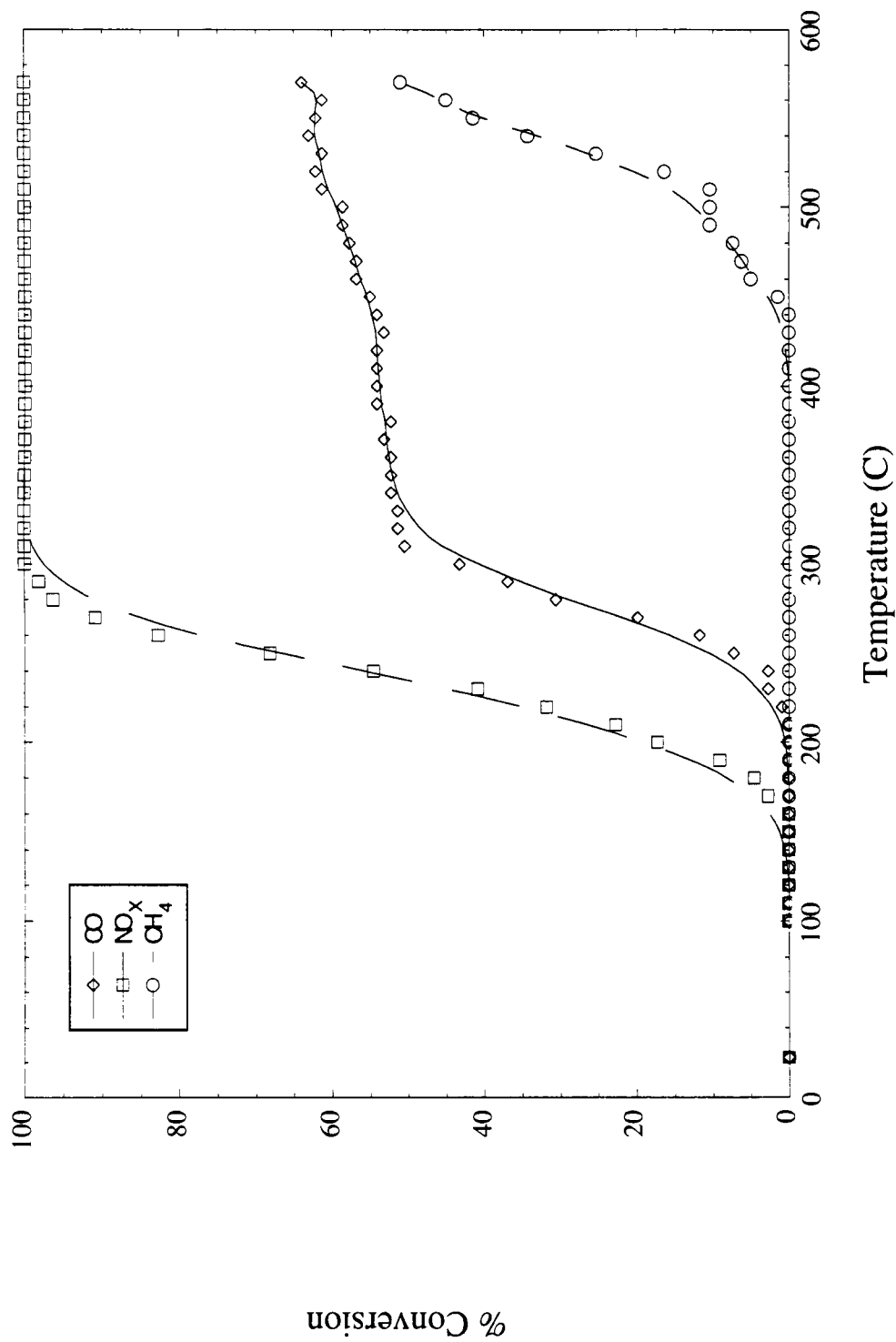


Figure A-24: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO for an Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Rich Noncycled Lightoff Test

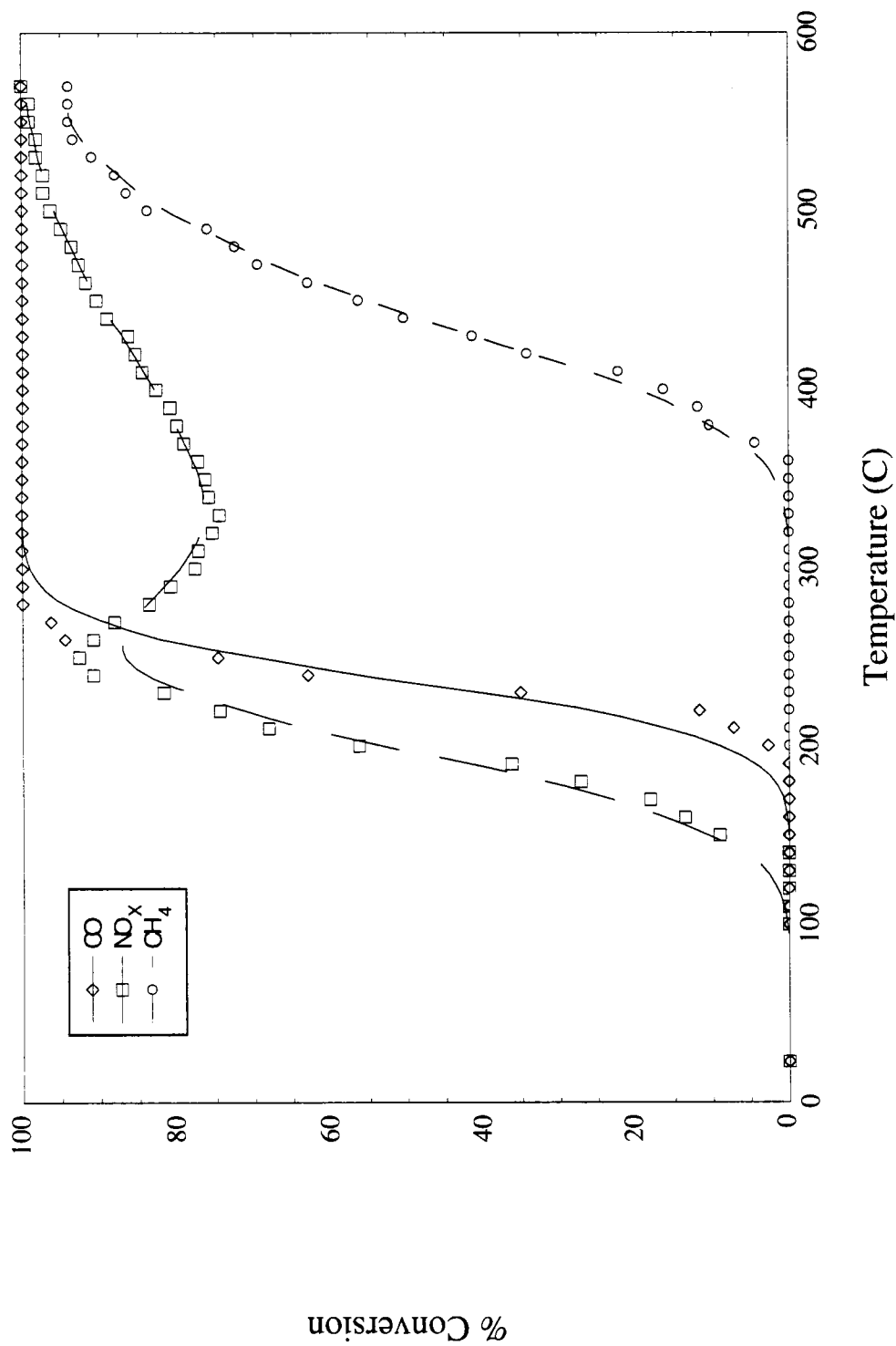


Figure A-25: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for an Aged Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3$  washcoat in a Stoichiometric Cycled Lightoff Test

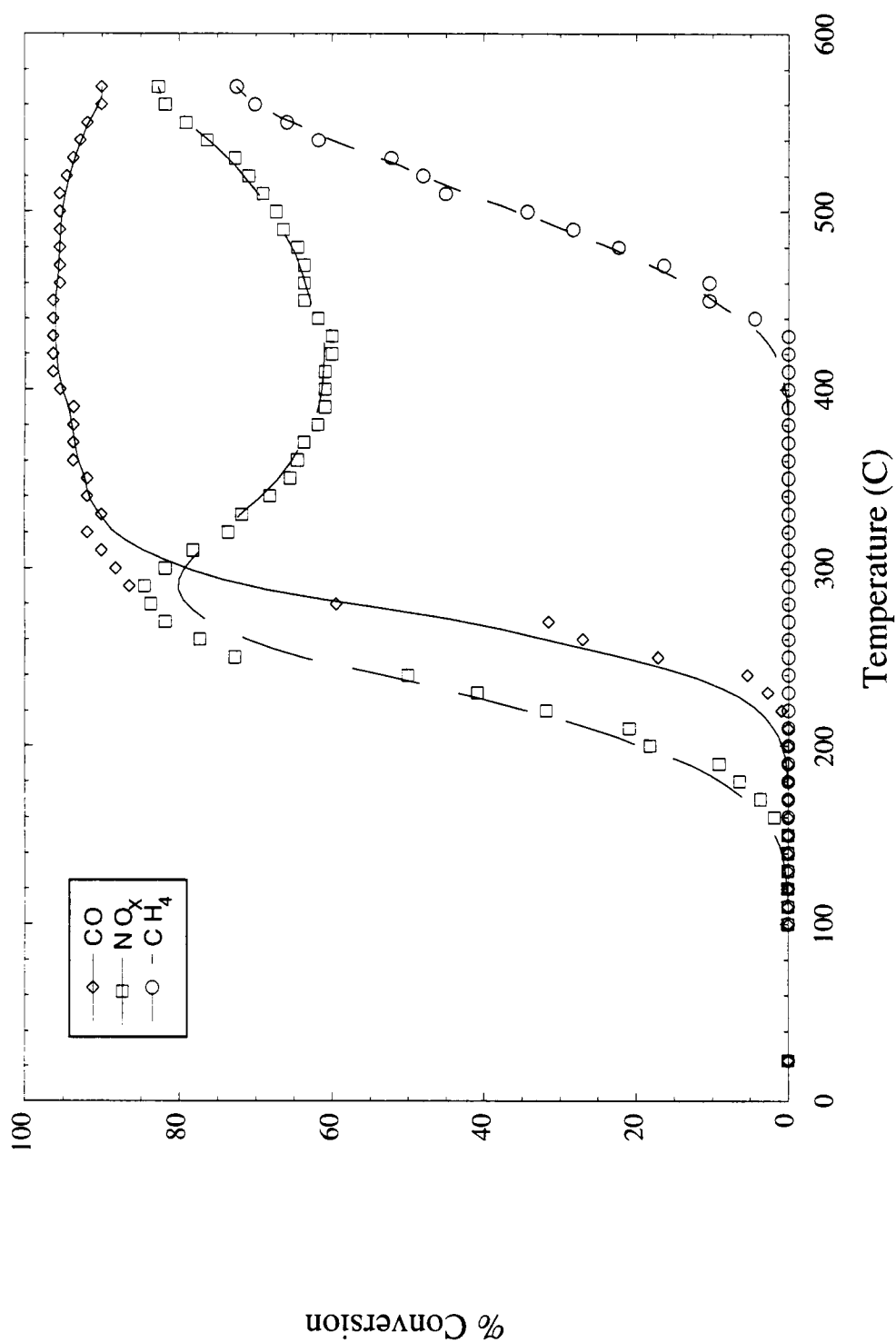


Figure A-26: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoichiometric Cycled Lightoff Test

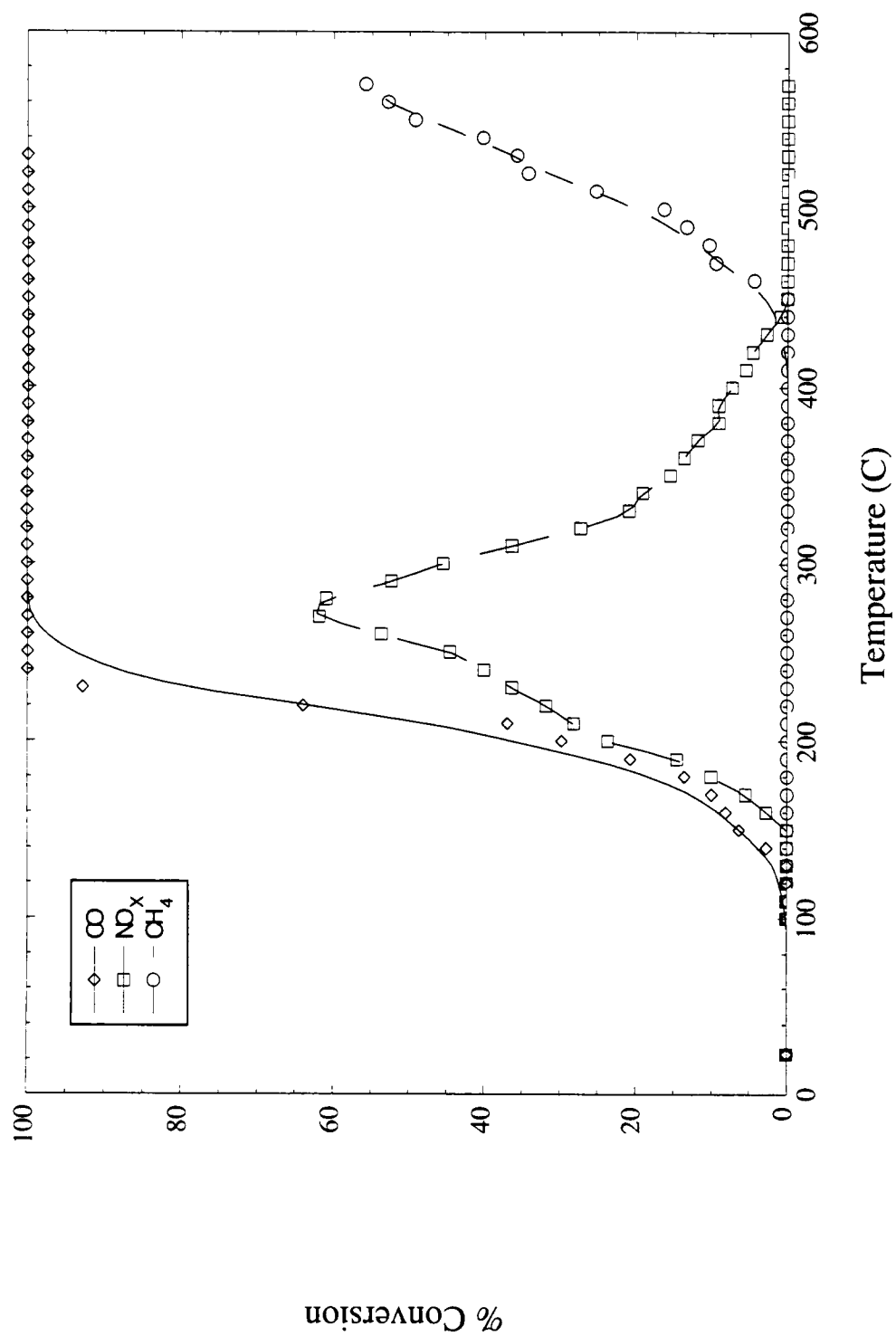


Figure A-27: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and CO for an Aged Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a Lean Noncycled Lightoff Test

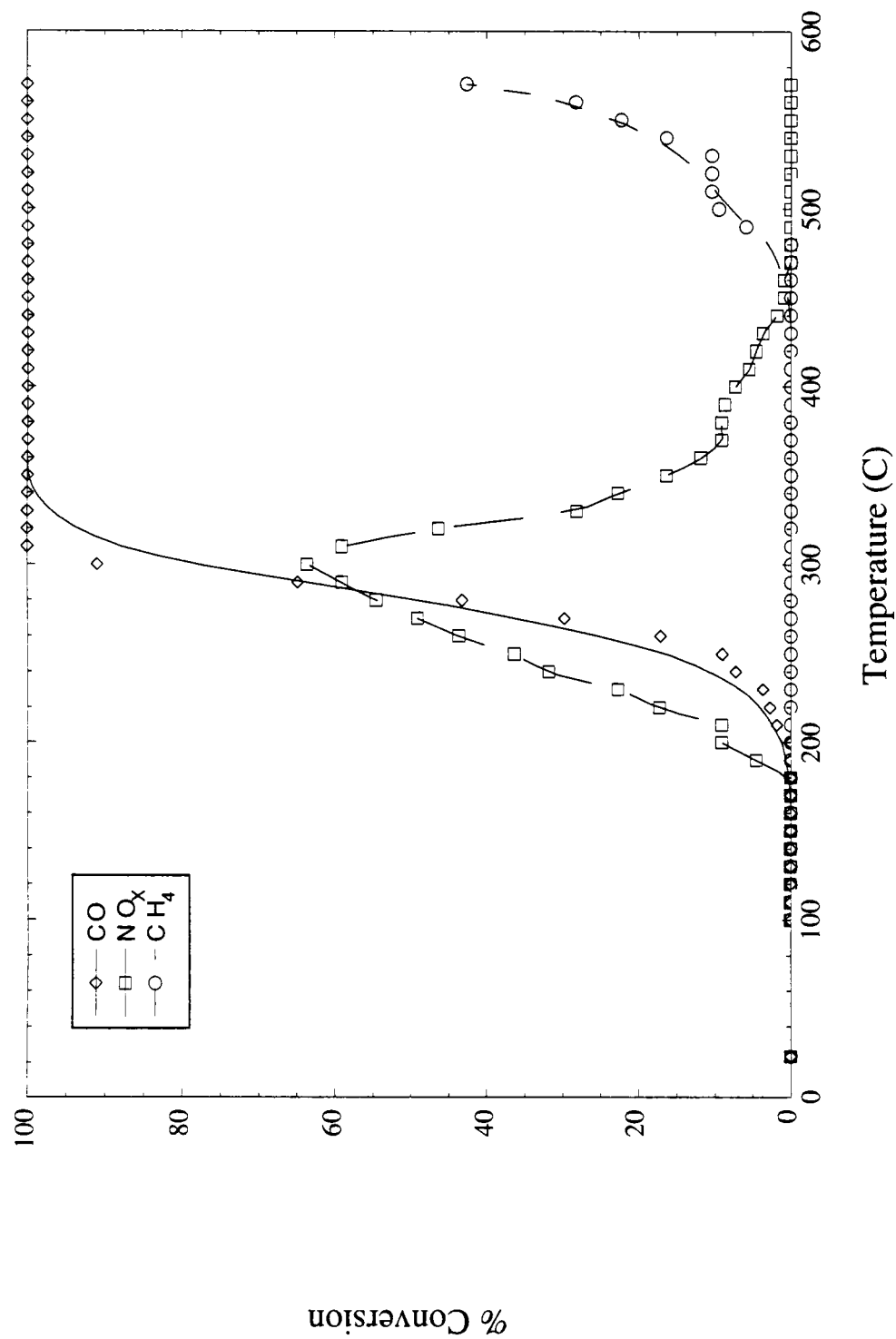


Figure A-28: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Lean Noncycled Lightoff Test

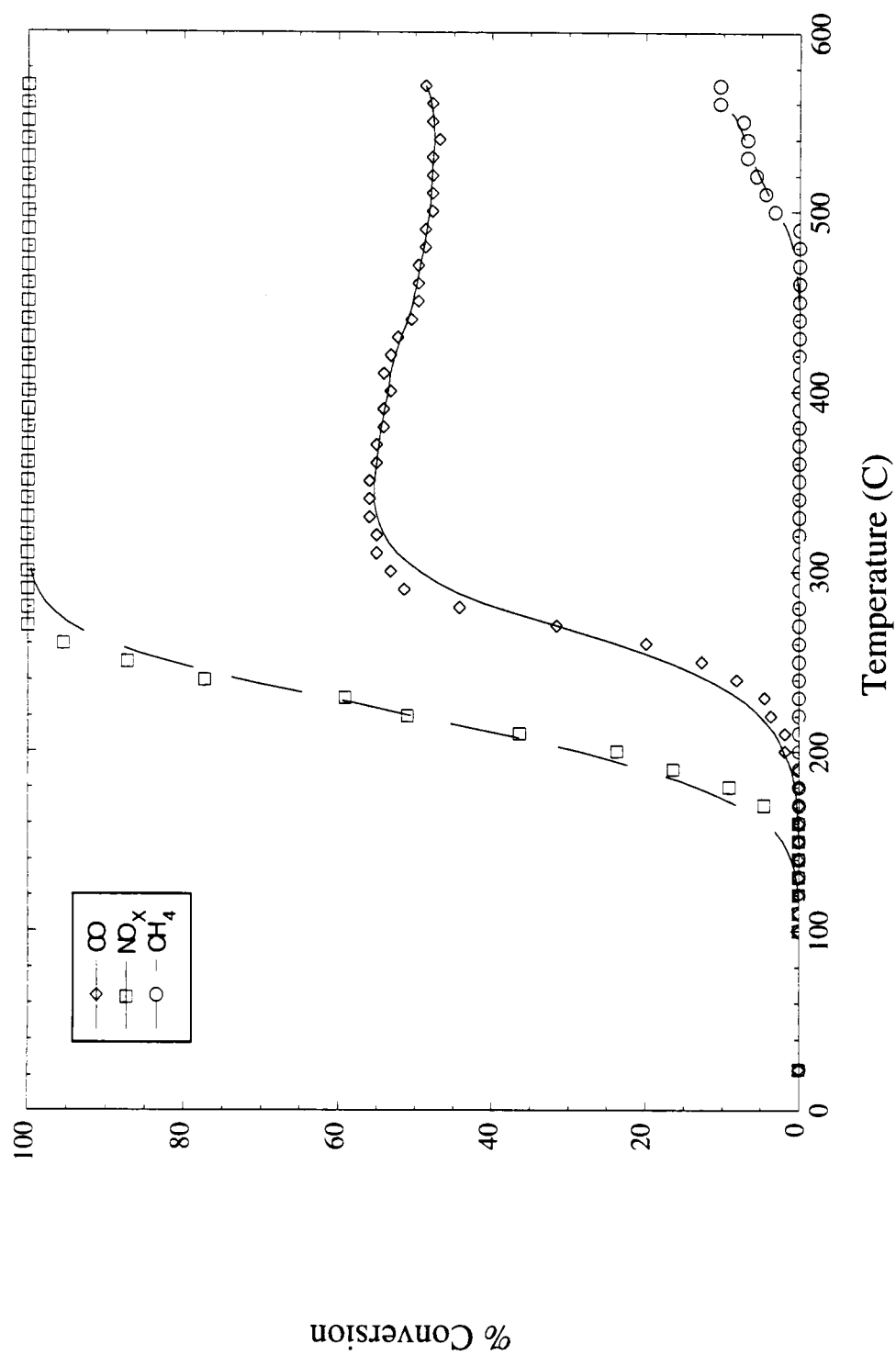


Figure A-29: Conversion Efficiencies of  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}$  for an Aged Catalyst with a  $60 \text{ g/ft}^3$  Pd/Rh loading and an  $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{La}_2\text{O}_3$  washcoat in a Rich Noncycled Lightoff Test

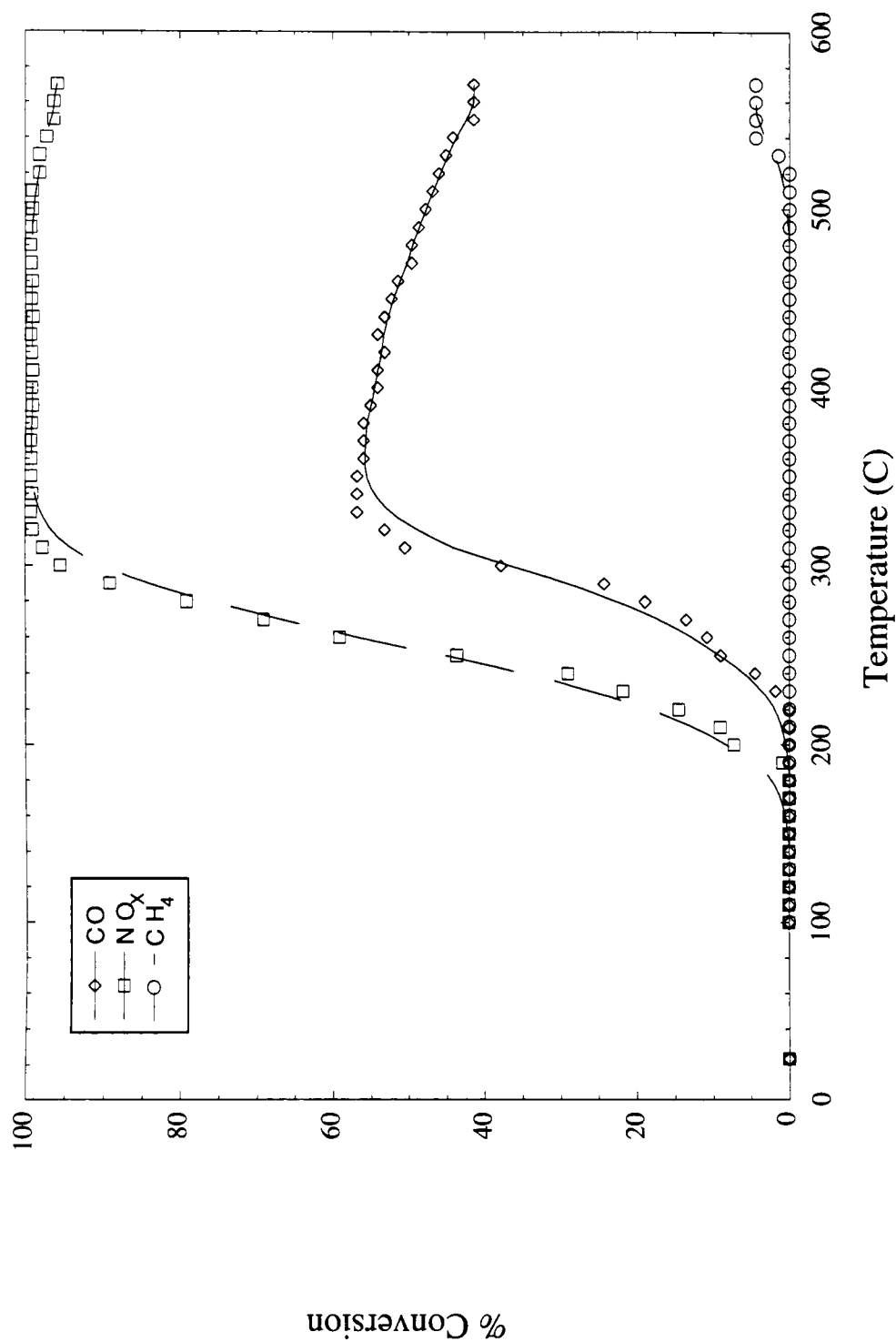


Figure A-30: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Rich Noncycled Lightoff Test

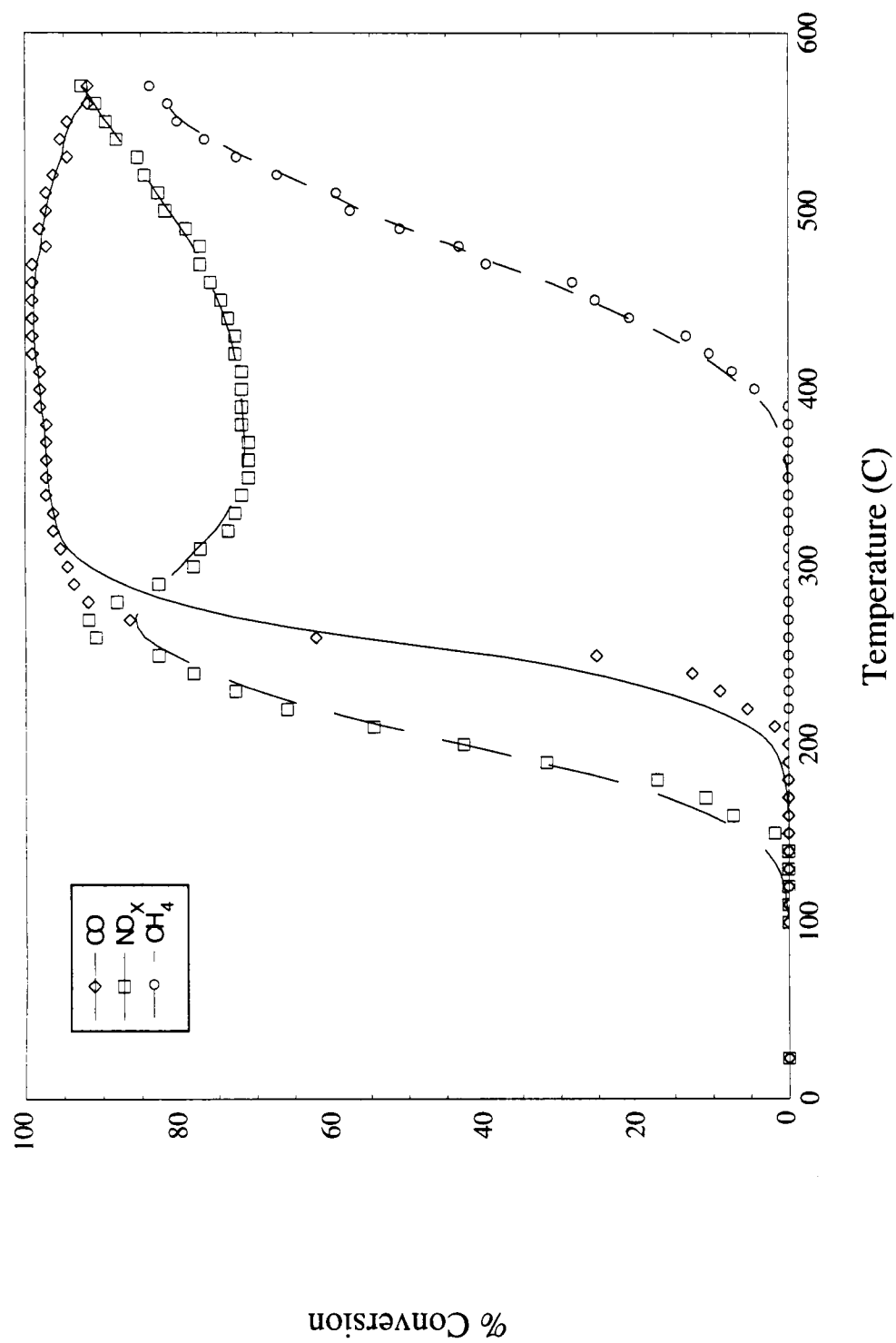


Figure A-31: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 60 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

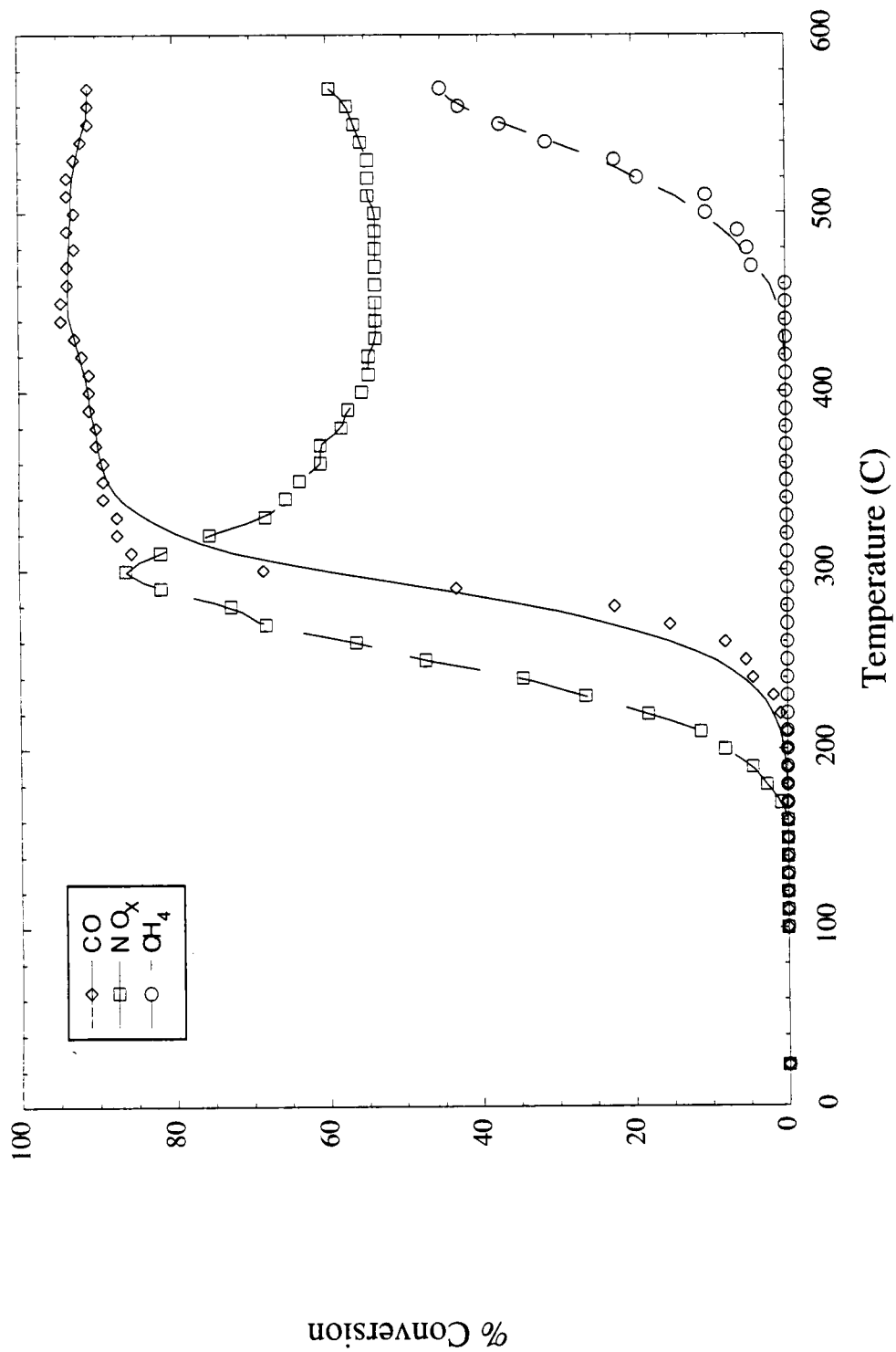


Figure A-32: Conversion Efficiencies of CH<sub>4</sub>, NO<sub>x</sub> and CO for an Aged Catalyst with a 10 g/ft<sup>3</sup> Pd/Rh loading and an Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/La<sub>2</sub>O<sub>3</sub> washcoat in a Stoich. Cycled Lightoff Test

Table A-1: Specifications for the Analyzers

| <b>AIA-2 Carbon Monoxide Analyzer:</b>              |                   |                                            |
|-----------------------------------------------------|-------------------|--------------------------------------------|
|                                                     | Accuracy          | 1%                                         |
|                                                     | Drift             | 1% full scale for 8 hours                  |
|                                                     | Speed of Response | 90% electronic response in 0.5 seconds     |
|                                                     | Sensitivity       | 0.5% full scale                            |
|                                                     | Output            | 0-5 volts for data acquisition             |
|                                                     |                   |                                            |
| <b>Beckman 951 NO/NOx Analyzer:</b>                 |                   |                                            |
|                                                     | Ranges            | 10, 25, 100, 250, 1000, 2500 and 10000 ppm |
|                                                     | Sensitivity       | 0.1 ppm on 10 ppm range                    |
|                                                     | Dynamic Response  | < 5 seconds on all ranges                  |
|                                                     | Linearity         | 1% of full scale                           |
|                                                     | Precision         | 0.5% of full scale                         |
|                                                     |                   |                                            |
| <b>Bendix Model 8402 Total Hydrocarbon Analyzer</b> |                   |                                            |
|                                                     | Range             | 0-1 ppm full scale                         |
|                                                     | Sensitivity       | 0.01 ppm                                   |
|                                                     | Precision         | 2% full scale                              |
|                                                     | Response time     | 8 seconds                                  |

Table A-2: Channel Listing

| Channel Listing                       | A/D | D/A |
|---------------------------------------|-----|-----|
| Bank A, CO                            | 0   | 0   |
| Bank A, H <sub>2</sub>                | 1   | 1   |
| Bank A, O <sub>2</sub>                | 2   | 2   |
| Bank A, N <sub>2</sub>                | 3   | 3   |
| Bank B, CO                            | 4   | 4   |
| Bank B, H <sub>2</sub>                | 5   | 5   |
| Bank B, O <sub>2</sub>                | 6   | 6   |
| Bank B, N <sub>2</sub>                | 7   | 7   |
| Bank C, CO <sub>2</sub>               | 8   | 8   |
| Bank C, SO <sub>2</sub>               | 9   | 9   |
| Bank C, NO                            | 16  | 0   |
| Bank C, C <sub>3</sub> H <sub>6</sub> | 17  | 1   |
| INLET                                 | 18  | 2   |
| OUTLET                                | 19  | 3   |
| REACTOR                               | 20  | 4   |
| Pre - Catalyst Temp                   | 40  | —   |
| Post - Catalyst Temp                  | 41  | —   |
| Steam Temp                            | 43  | —   |
| System Pressure                       | 44  | —   |
| Vent Pressure                         | 45  | —   |
| Reactor Pressure                      | 46  | —   |
| Analyzer Pressure                     | 47  | —   |
| CO analyzer                           | 48  | —   |
| NO analyzer                           | 49  | —   |

## VITA

Paul Lisenby was born in Church Hill, Tennessee on March 11, 1970. He entered the University of Tennessee in August 1988 and graduated with honors in the degree of Bachelor of Science in Mechanical Engineering in May 1993. While in college, he cooperated with Eastman Chemical, I.B.M. and the Central Intelligence Agency. While working with the Central Intelligence Agency, he traveled extensively throughout Asia, Eastern and Western Europe, Africa and the Middle East on various assignments. In August 1993, Paul began graduate studies at the University of Tennessee, Knoxville where he received the degree of Master of Science in Mechanical Engineering in December of 1995.