



400 COMMONWEALTH DRIVE, WARRENDALE, PA 15096-0001 U.S.A.

SAE Technical Paper Series

892095

Development of Non-Nickel Additives for Reducing Hydrogen Sulfide Emissions from Three-Way Catalysts

Jeffery S. Rieck, Wilson Suarez and Joseph E. Kubsh

W. R. Grace & Co.

Conn. Research Division

Columbia, MD

International Fuels and Lubricants
Meeting and Exposition
Baltimore, Maryland
September 25-28, 1989

Volkswagen Ex. 1006A
Volkswagen v. EmeraChem
IPR2014-01554

The appearance of the ISSN code at the bottom of this page indicates SAE's consent that copies of the paper may be made for personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay a \$5.00 per article copy fee through the Copyright Clearance Center, Inc., Operations Center, 27 Congress St., Salem, MA 01970 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale.

SAE routinely stocks printed papers for a period of three years following date of publication. Direct your orders to SAE Customer Service Department.

To obtain quantity reprint rates, permission to reprint a technical paper or permission to use copyrighted SAE publications in other works, contact the SAE Publications Group.



*All SAE papers are
abstracted and indexed in
the SAE Global Mobility Database.*

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISSN 0148-7191
Copyright 1989 Society of Automotive Engineers, Inc.

Positions and opinions advanced in this paper are those of the author(s) and not necessarily those of SAE. The author is solely responsible for the content of the paper. A process is available by which discussions will be printed with the paper if it is published in SAE Transactions. For permission to publish this paper in full or in part, contact the SAE Publications Division.

Persons wishing to submit papers to be considered for presentation or publication through SAE should send the manuscript or a 300 word abstract of a proposed manuscript to: Secretary, Engineering Activity Board, SAE.

Printed In USA

Development of Non-Nickel Additives for Reducing Hydrogen Sulfide Emissions from Three-Way Catalysts

Jeffery S. Rleck, Wilson Suarez and Joseph E. Kubsh

W. R. Grace & Co.

Conn. Research Division

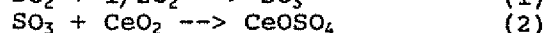
Columbia, MD

ABSTRACT

Under certain operating conditions, automotive three-way catalysts can form hydrogen sulfide in concentrations sufficient to produce an offensive odor. Several additives from the ferrite group of compounds ($M^{2+}Fe_2O_4$, where $M = Ni, Co, Zn, Cu$) have been determined to effectively reduce hydrogen sulfide emissions from three-way catalyst washcoats in laboratory tests. No alterations in the chemistry of the catalyst are required, and no detrimental effect on three-way activity is observed.

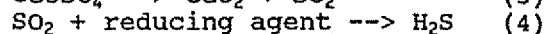
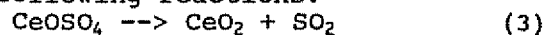
INCREASING ENVIRONMENTAL CONCERNS over emissions from automobiles have focussed attention on the durability of three-way catalytic convertors. High levels of rare earth oxides such as ceria and lanthana are incorporated into commercial three-way catalysts to improve long term catalyst performance and to provide more effective utilization of the noble metal components (1,2). However, increases in rare earth levels in commercial three-way catalysts have been accompanied by an increase in hydrogen sulfide production under certain transient conditions usually associated with changes in exhaust stoichiometry between lean and rich operations (3,4).

The mechanism for H_2S emissions associated with odor production is due to the storage and release of sulfur on the surface of three-way catalysts (3,5,6). The sulfur present in gasoline is oxidized to SO_2 during the combustion process. While the engine runs under lean conditions, sulfur can be stored on the catalyst surface by the following mechanism.



In the presence of platinum and other noble metals, reactions (1) and (2) are kinetically and thermodynamically favored for typical catalyst operating temperatures. Other rare earth oxides and alumina can contribute to the storage of sulfur by reaction (2).

Following a change in exhaust composition to a rich stoichiometry, the stored sulfur can be reduced to H_2S by the following reactions.



The reduction of the stored sulfur is catalyzed by noble metals (7). The reducing agent may be hydrogen, CO, or hydrocarbons present in the rich exhaust. While this process is shown as a two-step reaction, the surface sulfates may decompose directly into H_2S .

Several approaches have been developed to counter H_2S production by three-way catalysts. Deactivation of the support material by thermal treatments has some utility in decreasing the amount of sulfur stored (7). Sulfur storage may also be inhibited by incorporating additives such as phosphorus which poison the sites for sulfur storage (5,7). However, these approaches may have some drawbacks in terms of detrimentally affecting three-way catalyst performance. In addition, a technique for reducing H_2S emissions which necessitates an alteration of the catalyst support reduces flexibility in the development of new catalyst formulations.

An alternate approach is to incorporate an additive into the washcoat which reacts with H_2S under rich conditions to form a stable surface sulfide. The surface sulfide must then decompose under lean conditions to produce SO_2 ,

Table 1: Loadings of Catalyst Components^(a)

Substrate	Pt	Rh	Rare Earths ^(b)	H ₂ S Additives
M-metal	0.587	0.118	34.8	6.2
C-cordierite	1.47	0.294	17.7	14.4
C*-cordierite	1.47	0.294	34.8	14.4

(a) Loadings are given in g/liter.

(b) Rare earth loadings are sum of La₂O₃ and CeO₂.Table 2: Catalyst H₂S Additives

Sample	Substrate	H ₂ S Additive
C*	cordierite	none
C1	cordierite	none
C2	cordierite	NiO
C3	cordierite	NiFe ₂ O ₄
C4	cordierite	CoFe ₂ O ₄
C5	cordierite	ZnFe ₂ O ₄
C6	cordierite	CuFe ₂ O ₄
C7	cordierite	NiAl ₂ O ₄
C8	cordierite	CoAl ₂ O ₄
M1	metal	none
M2	metal	NiO
M3	metal	NiFe ₂ O ₄
M4	metal	CoFe ₂ O ₄

thereby regenerating the additive without the release of H₂S. Nickel oxide is an effective H₂S scavenger by this process (3) and is widely used in many commercial three-way washcoats. However, health concerns over nickel emissions from automotive catalysts have focussed attention on finding alternative additives that have similar performance to NiO but are environmentally benign. We have determined in our laboratory tests that certain ferrites (M²⁺Fe₂O₄) reduce H₂S emissions from three-way catalysts with the same utility as nickel. In addition, these materials have no effect on the activity of three-way catalysts.

EXPERIMENTAL

CATALYST PREPARATION - Pt/Rh three-way catalysts were prepared by washcoating cordierite and metal monolith substrates (62 and 50 cells/cm², respectively) with a lanthana-stabilized, γ-alumina-based washcoat. The noble metal and rare earth contents of the coated monoliths are given in Table 1. The catalysts in Table 1 include base case Pt/Rh washcoats and Pt/Rh washcoats incorporating Ni and ferrite additives. The Ni and ferrite additives were added to the washcoat as bulk oxides. The levels of these additives in the coated monoliths are also included in Table 1. The catalysts will be referred to according to the sample numbers given in Table 2.

H₂S EMISSIONS TESTING - H₂S emissions

Table 3: Laboratory H₂S Test Conditions

Component	Lean Condition	Rich Condition
CO	0.45	5.00
H ₂	0.15	1.67
C ₃ H ₆	0.03	0.03
C ₃ H ₈	0.01	0.01
O ₂	0.35	0.00
CO ₂	14.5	14.5
H ₂ O	13	13
SO ₂	0.0020	0.002
NO	0.185	0.185
N ₂	balance	balance
Temperature, C	550	550
Time, minutes	15	10
Catalyst Charge, cm ³		8.5
Gas Flow Rate, NTP Liter/min		2.83
GHSV		20,000

were measured using a laboratory reactor system developed by Ernest (8). A 8.5 cm³ catalyst sample was heated to 550 C and exposed to a lean simulated exhaust for 15 min. The catalyst was then exposed to a rich simulated exhaust for 10 min during which H₂S emissions were monitored using a Tracor Atlas Model 825RD analyzer. Up to four lean/rich cycles were performed until a reproducible quantity of H₂S was formed during the rich cycle. The H₂S test conditions are given in Table 3. H₂S emissions were determined for both fresh and laboratory aged catalysts described in Table 1.

ACTIVITY TESTING - Three-way activities were measured in the laboratory using a cycling reactor (9). In this test, conversions of hydrocarbons (HC), CO, and NO were measured over catalyst samples exposed to a simulated exhaust stream in which the concentrations of the oxidizing and reducing components were oscillated about a set point in order to simulate the cyclic behavior of real automobile exhaust streams. Catalyst activities were measured for several inlet gas compositions ranging from net oxidizing to net reducing. The composition of the simulated exhaust and other test conditions have been given elsewhere (9).

CATALYST AGING - Catalysts were subjected to two laboratory aging procedures

prior to testing for H_2S emissions and three-way activity. In the first aging protocol, catalysts were calcined in air for 4 hours at 980 C to simulate a high temperature exposure to an oxygen-rich exhaust stream. The second aging procedure simulated catalyst poisoning using a pulsated-flame aging system described elsewhere (9). In this pulsator test, a combustion stream formed by burning n-hexane doped with 800 ppm S, 70 ppm Pb, 112 ppm P, and 70 ppm Zn was passed over the catalyst. During this exposure, the catalyst temperature was cycled between 640 C for 90 minutes and 855 C for 15 minutes. This test is designed to approximate 80,000 km of vehicle service with 90 hours of pulsator aging.

RESULTS AND DISCUSSION

H_2S EMISSIONS: WASHCOATS CONTAINING NO ADDITIVES - Data showing the concentration of H_2S in the reactor effluent as a function of time during a rich cycle for the test protocol described in Table 3 are given in Figure 1 for fresh catalysts C* and C1, which contain no H_2S additives. Following the switch from lean to rich conditions, a large H_2S peak appears which decays to a steady-state value of approximately 20 ppm. This large peak results from the rapid release of sulfur stored on the catalyst surface during the lean portion of the test and its subsequent reduction to H_2S . The steady-state H_2S concentration of ca. 20 ppm results from the reduction of the 20 ppm of SO_2 present in the simulated exhaust feed. The H_2S odor produced by automotive catalysts under actual lean-rich cycling conditions should be closely related to the peak concentration of H_2S in the reactor effluent, and this peak concentration is the criterion by which we judge the effectiveness of H_2S additives.

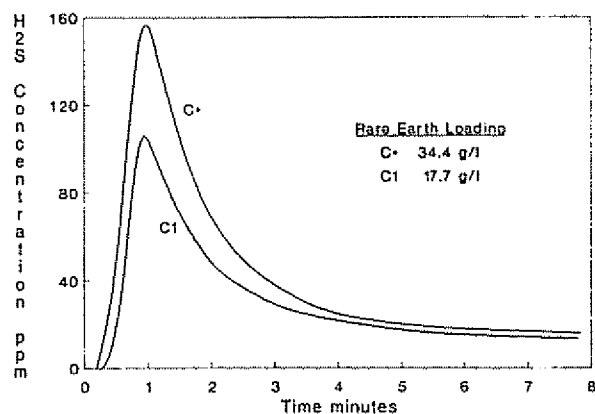


Figure 1: Effect of rare earth loading on hydrogen sulfide emissions.

As noted previously, high H_2S emissions have been linked to the high levels of rare earths in washcoats. The effect of rare earth loading on H_2S production from fresh catalysts containing no H_2S additive is shown in Figure 1. The peak H_2S concentration produced by sample C*, which contains 34.8 g/liter of rare earth oxides, is 157 ppm while the H_2S emission spectrum of sample C1, which contains 17.7 g/liter of rare earth oxides, reaches a peak of 106 ppm. This demonstrates that high rare earth levels are at least partially responsible for high H_2S emissions.

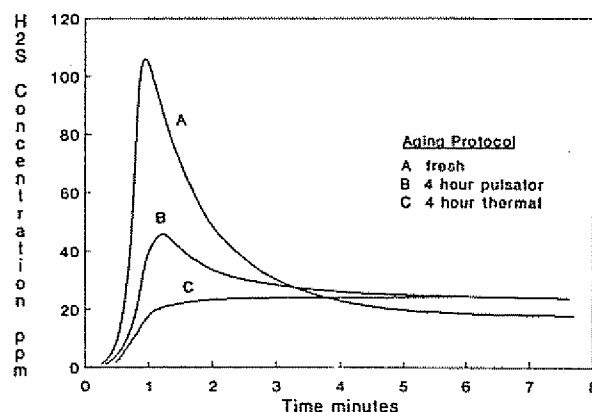


Figure 2: Effect of catalyst aging on hydrogen sulfide emissions.

As part of our effort to understand the factors governing H_2S production from three-way catalysts, an investigation of the effects of catalyst aging on H_2S emissions was undertaken. Figure 2 compares the H_2S emissions during a rich cycle from a fresh sample of catalyst C1 with that measured during a rich cycle for samples of catalyst C1 thermally-aged and pulsator-aged according to the protocols described previously. Following thermal aging, no H_2S peak is present. However, the thermally-aged sample still produces 20 ppm of H_2S at steady-state. This indicates that the absence of the H_2S peak is due to a decrease in the quantity of stored sulfur. Since the surface area and morphology of the lanthana-stabilized alumina support ($135 \text{ m}^2/\text{g}$) is not affected by this particular thermal treatment, it is unlikely that the lower quantity of sulfur stored is due to a decrease in the number of sites for sulfur adsorption. However, thermal aging decreases the noble metal dispersion of this catalyst as measured by CO chemisorption from 80% to 9%. Therefore, the absence of the H_2S peak for the thermally-aged sample is thought to result from a decrease in the activity for SO_2 oxidation due to noble metal sintering.

Figure 2 demonstrates that poisoning the catalyst surface by pulsator aging for 4 hours (equivalent to ca. 3300 km of operation) decreases the height of the H_2S peak from 106 ppm to 46 ppm. This agrees with the published observations that H_2S emissions from catalytic converters diminish with increasing time on-stream or increasing levels of typical poisons present on the catalyst (4,5,7). This decrease in H_2S production is due to a decrease in the amount of sulfur stored on the support due to blockage of sites for sulfur adsorption by the poisons in the exhaust stream.

The results of these aging studies show that H_2S production can be strongly influenced by alterations of either the noble metal dispersion or the chemistry of the support. However, these alterations also affect the three-way activity of the catalyst. Therefore, our approach has been to identify additives which reduce H_2S emissions without changes to the chemical nature of the catalyst itself.

H_2S EMISSIONS: H_2S ADDITIVES - Ferrites ($M^{2+}Fe_2O_4$; $M = Ni, Co$, etc.) have been evaluated as adsorbents for the removal of H_2S from high temperature gas streams (10). Studies have shown that a metal ferrite has the same capacity for sulfide adsorption as the pure metal oxide and that ferrites may regenerate more readily in oxidizing atmospheres to produce SO_2 than the metal oxide itself. Based on these results, we investigated the effectiveness of several ferrites including $NiFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$, and $CuFe_2O_4$ as H_2S scavengers in three-way catalyst formulations versus the commercial NiO additive.

Figure 3 compares the H_2S emissions following a rich cycle in our test protocol for fresh catalysts C1 through C6. As expected and consistent with data from other laboratories, the catalyst contain-

ing NiO (C2) produces no H_2S peak. For the ferrite-containing washcoats, a range in reductions in H_2S peak emissions is exhibited in Figure 3 dependent on the nature of the M^{2+} cation present in the ferrite matrix. $ZnFe_2O_4$ (C5) exhibits only limited reductions in peak H_2S concentrations versus the base case three-way catalyst, C1. The $NiFe_2O_4$ additive (C3) shows H_2S emissions intermediate between the NiO system and the base case catalyst. However, it is important to note that catalyst C3 contains only 30% as many Ni atoms as contained in C2 due to the dilution of nickel by iron in the ferrite matrix. The $CoFe_2O_4$ (C4) and $CuFe_2O_4$ (C6) additive systems exhibit H_2S emission levels similar to that of the NiO -containing catalyst. Both $CoFe_2O_4$ - and $CuFe_2O_4$ -containing washcoats produce significant reductions in peak H_2S emissions versus the base case three-way catalyst.

Samples of catalysts C1 through C4 were also tested for H_2S emissions following the two aging protocols described previously. Table 4 gives the H_2S peak heights for these catalysts for fresh, thermally-aged, and 4 hour pulsator-aged samples. These results demonstrate that catalyst aging does not affect the H_2S removal efficiency of the ferrite-containing washcoats.

In addition to ferrites, aluminates ($M^{2+}Al_2O_3$) have also been demonstrated to be effective adsorbents for H_2S (10). To develop a better understanding of the ability of sulfur adsorbents to control H_2S emissions in automotive environments, three-way catalysts containing $NiAl_2O_3$ (C7) and $CoAl_2O_3$ (C8) additives were tested for H_2S emissions. The results for these catalysts are included in Table 4. Unlike their ferrite counterparts, neither $NiAl_2O_3$ nor $CoAl_2O_3$ have any effect on the production of H_2S from three-way catalysts during our lean/rich laboratory cycles. The observed H_2S behavior of these aluminates parallels other data on the catalytic oxidation characteristics of aluminates versus their corresponding bulk oxides. For example, nickel oxide has significant oxidation activity for CO or hydrocarbons while $NiAl_2O_3$ has been shown to have little or no oxidation activity (11). Reasons for this observed activity difference are not well understood, but it would not be unreasonable to expect that similar matrix effects would be important in the ability of a divalent cations such as Ni^{2+} to form a stable surface sulfide in the presence of H_2S . The ferrite matrix appears to provide a local electronic and/or structural environment that facilitates the formation of this surface sulfide while the aluminate matrix does not.

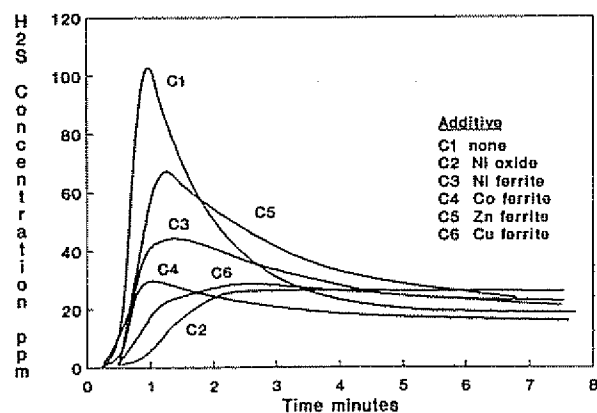


Figure 3: Effect of additives on hydrogen sulfide emissions; cordierite substrate.

Table 4: H₂S Emissions from Specified Catalyst Washcoat

Catalyst	H ₂ S Peak Emissions (ppm)		
	Fresh Sample	Samples aged at 980 C for 4 hours in air	Samples aged in the presence of exhaust poisons for 4 hours
C1	106	25	46
C2	26	17	21
C3	44	17	20
C4	30	18	18
C7	99		
C8	118		

The observed lack of H₂S gettering ability of the aluminates tested here also points out the need for minimizing interactions between the additive and the alumina-based active catalyst. Interactions could lead not only to losses in catalyst activity but also in the additive's ability to effectively scavenge H₂S produced during rich transients due to the formation of aluminates at higher operating temperatures.

As touched upon above, the divalent cation, M²⁺, present in the ferrite matrix is thought to be the site in the ferrite which forms the stable surface sulfide in the presence of H₂S. The trend observed in Figure 3 for the ferrite-containing catalysts may be related to the relative stability of the sulfide and sulfate M²⁺ surface complexes that form under rich and lean stoichiometries, respectively. For example, in comparing the thermodynamic stabilities of bulk sulfides and sulfates of Zn, Ni, Cu, and Co, one finds that the trend is Zn > Ni > Co = Cu. This is consistent with the observations of Figure 3 in which ZnFe₂O₄ is the least effective H₂S getter followed by NiFe₂O₄, CoFe₂O₄, and then CuFe₂O₄. The formation of relatively stable surface sulfates under lean conditions or relatively stable surface sulfides under rich conditions may limit the ability of the M²⁺ cation to

effectively remove H₂S under cyclic conditions, where a surface sulfide must be both formed and released to regenerate the active getter site.

Following these investigations of ferrite additives, additional samples were prepared on a metal monolith substrate (M1 through M4) with a 60% reduction in the level of the ferrite additive and twice the amount of rare earth oxides contained in the cordierite samples of Table 1. As shown in Figure 4, the ferrite additives are still effective at decreasing H₂S production at these higher ratios of rare earth components to ferrite additives.

ACTIVITY TESTING - In order to identify any detrimental effects of the ferrite additives on catalyst performance, catalysts C1 through C4 were tested in the laboratory for three-way activity following thermal aging and 90 hours of pulsator aging. The results are shown in Table 5 along with activity data for fresh catalyst samples. These data show that the catalysts containing the ferrite additives CoFe₂O₄ and NiFe₂O₄ have essentially equivalent aged three-way performance in comparison to the base-case Pt/Rh washcoat.

CONCLUSIONS

The results presented allow the following conclusions to be reached.

Increasing the loading of rare earth oxides in three-way catalysts contributes to an increase in the quantity of H₂S produced during oxygen deficient transients by providing more sites for sulfur storage on the catalyst surface.

Sintering of the noble metals on three-way catalysts reduces H₂S emissions, presumably by decreasing the activity of the catalyst for SO₂ oxidation and thereby decreasing the quantity of sulfur stored.

Poisoning of the catalyst with P, Pb, and Zn decreases the quantity of H₂S produced by blocking sites on the support for sulfur storage.

Ferrite additives such as NiFe₂O₄,

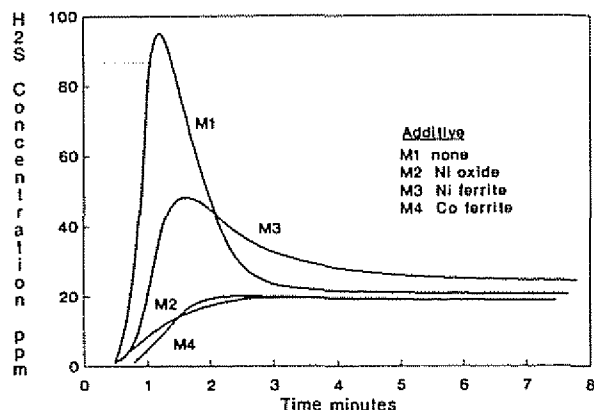


Figure 4: Effect of additives on hydrogen sulfide emissions; metal substrate.

Table 5: Three-way Catalyst Activities (% conversions)

Sample	$\lambda = 1.006$			$\lambda = 0.999$			$\lambda = 0.993$		
	HC	CO	NO	HC	CO	NO	HC	CO	NO
Fresh									
C1	95	93	81	93	89	94	93	82	85
C2	93	93	82	93	89	95	93	81	86
C3	96	93	80	92	87	93	92	81	85
C4	95	93	82	93	87	93	93	82	85
980 C, 4 h in air aged									
C1	82	72	67	79	63	72	75	54	74
C2	75	71	67	70	66	71	62	56	76
C3	81	71	63	77	65	68	72	58	71
C4	86	71	67	82	62	71	76	52	74
90 h pulsator aged									
C1	80	68	63	77	65	71	71	51	66
C2	81	63	63	73	63	70	69	50	65
C3	80	68	64	80	70	66	74	56	73
C4	80	67	62	76	63	67	71	58	72

CoFe₂O₄, and CuFe₂O₄ are as effective as NiO at reducing H₂S emissions from three-way catalysts containing significant levels of rare earth promoters. Reductions in peak H₂S emissions during a rich transient are maintained for ferrite-containing washcoats subjected to typical laboratory aging protocols. Three-way activity of washcoats containing NiFe₂O₄ and CoFe₂O₄ is on a par with Pt/Rh washcoats containing no H₂S additives. These ferrite additives have also been shown to be equally effective on both cordierite and metal foil substrates.

ACKNOWLEDGEMENTS

The authors would like to thank Jeffrey DeBoy, Joe Vaccarino, Keith Halle, all of the Research Division, and Mike Ernest of W.R. Grace's Davison Division for help in preparing and evaluating catalyst samples described in this paper.

REFERENCES

1. W.B. Williamson, J.C. Summers, and J.F. Skowron, SAE Paper 88013 (1988).
2. M. Bettman, R.E. Chase, K. Otto, and W.H. Weber, J. Catalysis, 117, 447 (1989).
3. M.G. Henk, J.J. White, and G.W. Denison, SAE Paper 872134 (1987).
4. I. Gottberg, E. Hogberg, and K. Weber, SAE Paper 890491 (1989).
5. A.F. Giwell, C. Hallet, and J.R. Taylor, SAE Paper 872163 (1987).
6. T.J. Truex, H. Windawi, and P.C. Ellgen, SAE Paper 872162 (1987).
7. E.S. Lox, B.H. Engler, and E. Koberstein, SAE Paper 890795 (1989).
8. M.V. Ernest, to be presented at SAE Int. Fuels and Lubricants Meeting, Baltimore, MD, Sept. 1989.
9. M.V. Ernest and G. Kim, SAE Paper 800083 (1980).
10. S.S. Tamhankar, M. Bagajewicz, G.R. Gavalas, P.K. Sharma, and M. Flytzani-Stephanopoulos, Ind. Eng. Chem. Process Des. Dev., 25, 429 (1986).
11. B.J. Cooper and L. Keck, SAE Paper 800461 (1980).