

DEVELOPMENT OF IMPROVED Pd-ONLY AND Pd/Rh THREE-WAY CATALYSTS

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ABSTRACT

The results of a development program for Pd-only and Pd/Rh automotive emission control catalysts are discussed. A review of former experiences with Pd-containing systems, especially their poor tolerance against lead and sulfur poisoning is given. Model gas experiments were conducted with improved Pd-based catalysts. Not only the activity to convert simultaneously CO, NO_x and hydrocarbons (HC) was investigated, but also the formation of so-called secondary emissions such as N₂O or NH₃.

The catalyst development was supported by XPS-measurements paying special attention to the oxidation state, spread and the dispersion of Pd. Promising Pd and Pd/Rh-catalyst candidates were tested fresh and after engine aging on engine- and vehicle dynamometers. The results are compared to Pt/Rh-catalysts. For Pd-only catalysts the ratio of catalyst volume to vehicle mass seems to be one important factor to guarantee high conversion levels after aging. The Pd/Rh-technologies reported in this study showed similar activities on different vehicles and in different test cycles as Pt/Rh catalysts. With the new developed Pd/Rh-catalyst the European legislation for model year 1996 could be achieved thus representing an economical and technical alternative to Pt/Rh-catalysts. Major potential for further improving the Pd/Rh-technologies performance must be seen in an optimization work regarding fuel quality and A/F-management.

1. INTRODUCTION

The majority of modern gasoline fueled passenger cars is equipped with so-called closed-loop three-way catalysts to aftertreat their exhaust gases [1]. The purpose of this system is to convert simultaneously carbon monoxide, hydrocarbons and nitrogen oxides by means of a precious metal based heterogeneous catalyst, whereby the engine's air-to-fuel-ratio is controlled to

obtain exhaust gas compositions that guarantee optimal conversions. For a long time Pt/Rh-containing converters were dominant, but there is a growing interest for using Pd in such catalysts for several reasons described in what follows:

First of all, economic factors have to be mentioned, because for the time being Pd is by far the cheapest precious metal that is applicable in automobile converters, see [Figure 1](#).

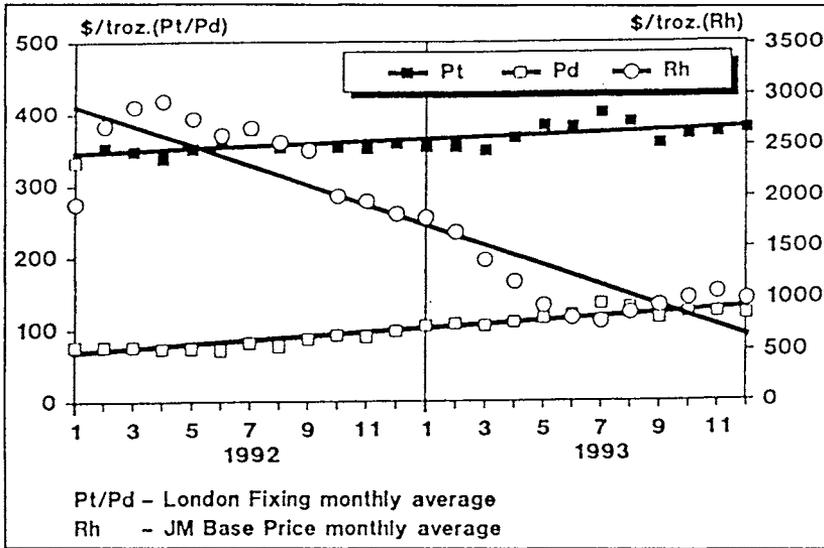


Figure 1: Pt, Pd and Rh monthly average prices in 1992 and 1993 [2].

But on a long term basis a major increase of the amount of Pd used in automobile converters might change the price situation completely. Indeed, presently only 9 % of the Pd available to the market is used in automotive emission control catalysts. In case of Pt this share is about 45 %, whereas the world supply of Pt and Pd is in the same order of magnitude, see [Figure 2](#).

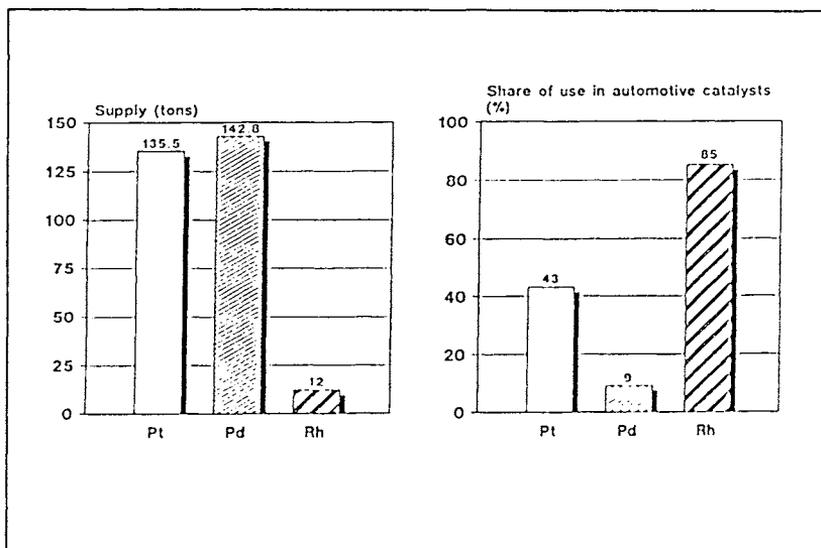


Figure 2: World supply of Pt, Pd and Rh in 1992 and share of automotive catalyst application [2].

Second, technical boundary conditions have been improved, such as the sulfur and lead content in the fuel. They limited in former times the use of Pd as precious metal component for high performance three-way catalysts [1]. Additional deposits of oil ashes caused major activity losses for Pd. Furthermore the A/F-window for Pd-containing catalysts was limited due to irreversible damage for the oxidation reactions and for the reduction of NO_x under rich conditions by SO_2 . Besides this the literature reports that higher levels of secondary emissions like NH_3 and N_2O could be formed [3-7]. Next, Pd and Rh containing catalysts are more sensitive to lead poisoning than Pt-containing catalysts due to a bulk alloy or solid solution formation between Pd and lead. Several investigations have covered these findings [8, 9].

Due to a number of improvements in fuel quality, significantly lower lead and sulfur contents and improved engine management systems, Pd-containing catalysts gain more and more interest.

In the last 10 years the gasoline sulfur and lead content in Europe and the United States decreased significantly. Table 1 illustrates the situation [7, 11].

Table 1: Development of the fuel sulfur and lead content

Country	Sulfur content [ppm]	Country	Lead content [g/l]
USA (ASTM unleaded, 7-7-1986) ^a	1000	USA (1985/86)	0,013
Field USA	40 - 300	Field USA (1985/86)	0,29 0,13 0,026
		Today	≤ 0,001
FRG (DIN 51607, August 1989)	1000	FRG (since 1989)	0,013
Field FRG (today)	50 - 450 ppm	Field FRG	≤ 0,003

^a) EPA § 86.1213-87, fuel specifications

In Germany nowadays a span of sulfur levels between 50 and 450 ppm is detected in the field. The usual values range below 150 ppm. In Germany the lead content of unleaded fuel reaches values below 3 ppm.

To meet the more stringent emissions standards especially for Europe and the U. S. not only a tighter A/F-control around stoichiometry is implemented, but also in many cases secondary air is added to the exhaust gas to achieve a quicker light-off. Under such conditions Pd-containing converters also were reported to have advantages over state-of-the-art Pt/Rh-catalysts [7, 10, 12].

Summarizing there are both economic and technical reasons to explain the growing interest in Pd-containing catalytic converters to reduce automobile emissions. Main results of a long term development program are shown in this study.

2. EXPERIMENTAL

2.1 Catalysts

The catalyst samples were prepared by coating monolithic cordierite substrates with a cell density of 400 cpsi and a wall thickness of 6.5 mil with an aqueous slurry of different aluminum oxides containing certain stabilizers together with state-of-the-art as well as special stabilized oxygen storage components. The washcoat loadings ranged between 140 and 250 g/l catalyst. After drying and calcining the washcoated monoliths (700°C, 2 h, static air) the samples were impregnated with aqueous solutions of the desired amount and kind of precious metals, followed by drying, calcination and reduction steps. The precious metal loadings varied from 80 to approx. 1100 g/ft³ for Pd, 40 to 50 g/ft³ for 5Pt/1Rh, and 40 to 90 g/ft³ for 5 Pd/1Rh. Parts of the catalysts were evaluated fresh and after different aging procedures in model gases (air, 4 h, 1050°C) or in real engine exhaust gases (fuel cut aging cycles, catalyst inlet temperatures between 870 and 950°C, 40 to 100 hours).

The model gas studies were performed with samples of 1 inch diameter and 3 inch length, for engine tests pieces of 1.5 inch diameter and 6 inch length were drilled out of larger samples. In the vehicle tests the ratio of catalyst volume to engine displacement ranged between 0.7 and 1.5.

2.2 Activity Test Procedures

2.2.1 Model Gas Tests

Different types of model gas tests were performed. Standard light-off and dynamic sweep test methods were applied for the activity comparison [13], furthermore the formation of secondary emissions such as NH₃ and N₂O was investigated in separate test cycles [14]. Parts of the tests were performed with SO₂-free and others with SO₂ containing gas mixtures.

2.2.2 Engine Tests

The engine performance tests were conducted on dynamometers equipped with EFI (Electronic Fuel Injection) gasoline engines using different types of light-off tests and A/F-scans. The space velocity was kept constant at 60.000 NI/h. The exhaust gas composition for the light-off tests varied from about stoichiometry over slightly lean to a very lean composition, during the A/F-scans the perturbation frequency as well as the amplitude was changed. Details are given in [15, 16].

2.2.3 Vehicle Tests

The vehicles used in this study are developed for the current US or EU legislation. The engine displacements ranged from 1.3 to 3.2 liters (EFI engines using 4 to 8 cylinders). European and US driving cycles were applied, the fuel corresponded to current US and EU specifications.

2.3 Catalyst Characterization

Surface analysis investigations (XPS) were performed on a Leybold equipment already described in [16]. The fresh catalyst samples were stored under argon prior to the catalytic tests and the surface analysis. The aged catalyst samples were also handled under argon. The precious metal dispersion was determined for some of the catalysts by a pulsed CO chemisorption technique [16].

3. TEST RESULTS

As already reported the main drawbacks for the introduction of Pd-based three-way catalysts are their smaller A/F-window and their insufficient resistance against sulfur poisoning. To overcome these disadvantages a research program was conducted that first concentrated on a washcoat development using model gas activity tests for Pd-only catalysts. Based on these results engine tests followed by vehicle tests were performed with Pd/Rh- and partwise with Pd-only technologies.

3.1 Model Gas Test Results

In lean and rich model exhaust gases activity tests were performed with different Pd-only catalysts and compared to a Pt/Rh-reference system based on a $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ washcoat. Parts of the results are illustrated in [Figure 3a](#) and [3b](#).

[Figure 3a](#) gives the light-off temperatures for CO and HC, determined at a 50 % conversion of the pollutant. Under oxidizing as well as under reducing conditions a new developed stabilized washcoat containing modified Al_2O_3 , special oxygen storage components and certain promoters showed by far the best light-off behaviour. Alumina-only based Pd-catalysts had approx. a 80°C higher light-off temperature.

A similar conclusion is reached from [Figure 3b](#), where the dynamic conversion level for CO and NO_x are plotted. Here the $\text{Al}_2\text{O}_3/\text{Pd}$ -catalysts fail

totally, whereas the stabilized washcoat/Pd-system performs similar as compared to the Pt/Rh-based catalyst, even after aging. The high NO_x -conversions especially under rich conditions for the best Pd-only technology are remarkable.

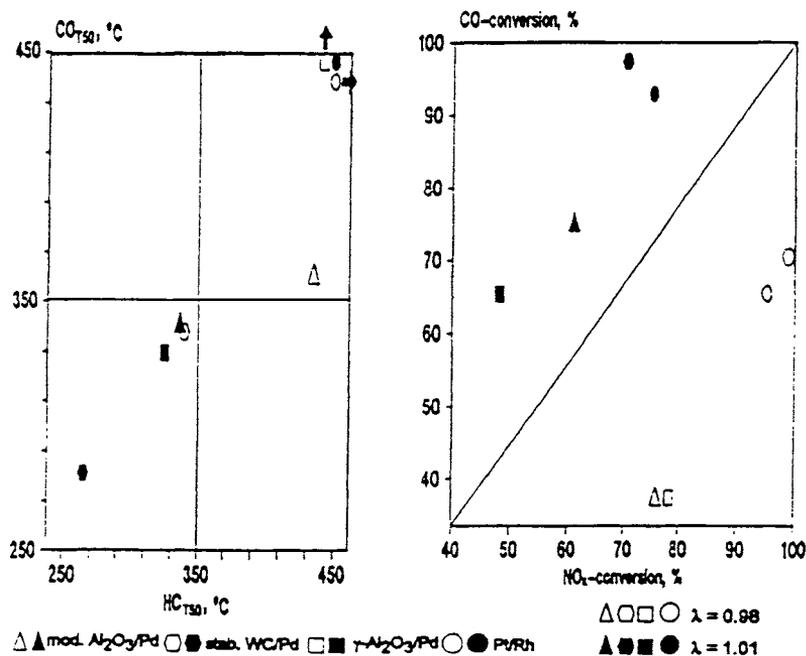


Figure 3: Model Gas Test Results - Comparison of 5Pt/ 1Rh (40 g/ft³) with Pd-only (80 g/ft³, 4h, 1050 °C, air aged)
 a) light-off test, $\text{SV} = 50.000 \text{ h}^{-1}$
 b) A/F-scan, $\text{SV} = 50.000 \text{ h}^{-1}$, $T = 400 \text{ }^\circ\text{C}$

Next the influence of SO_2 on the activity was investigated for the Pt/Rh- and the best Pd-only catalyst. Figure 4 reports the conversion rates for HC (Figure 4 a) and NO_x (Figure 4 b) for different temperatures in a rich gas atmosphere.

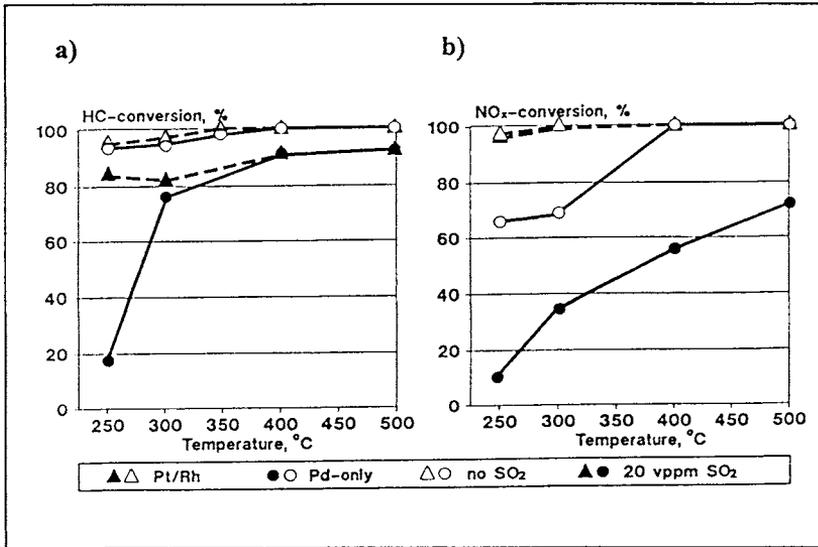


Figure 4: Model Gas Test Results - Comparison of 5Pt/1Rh (40 g/ft³) with Pd-only (80 g/ft³) catalysts; (SV = 50.000 h⁻¹, A/F = 14.45, fresh catalysts)

In the sulfur-free gas mixture the Pd-only catalyst already shows disadvantages for NO_x at temperatures below 350° C, and this becomes even more pronounced in the experiment with SO₂-containing gas. For HC differences are only obvious at temperatures below 300° C. But for sure these results indicate again the strong influence of sulfur on the performance of Pd-only catalysts.

Another interesting question that is raised regarding automotive catalytic converters is the formation of secondary emissions. In this study main emphasis was put on the nitrogen containing molecules NH₃ and N₂O, the latter of which becomes more and more important due to it's green house effect potential. First the NH₃-formation is compared for the Pt/Rh- and the stabilized Pd-system, see Figure 5.

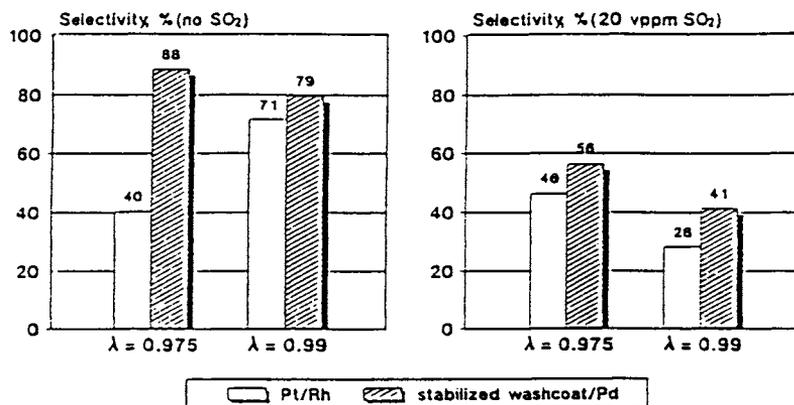


Figure 5: Model Gas Test Results - Comparison of 5Pt/1Rh (40g/ft³) with Pd-only (80g/ft³); Formation of NH₃ (T=300°C, SV=50.000h⁻¹, fresh catalysts);

Under the test conditions reported the selectivity S for the formation of NH₃, defined as

$$S_{NH_3} = \frac{n_{NH_3, out}}{n_{NO_x, in} - n_{NO_x, out}} \quad (n = \text{molar flow of the component}) \quad (1)$$

is always more pronounced for the Pd-only catalyst. This is true for both SO₂-free and SO₂-containing gas mixtures and confirms data reported already in chapter 2. The influence of the temperature and the A/F-ratio on the selectivity is nearly negligible up to a temperature of approx. 400°C under rich conditions (A/F from 14.24 to 14.45). This might be of importance for vehicles operating rich during cold-start, where Pd-based converters might form larger amounts of NH₃ as compared to Pt/Rh. The conversion of NO_x was comparable in the SO₂ free gas mixture; in the presence of SO₂ the Pd-only system lost somewhat in performance.

The formation of N₂O for the same catalysts at A/F = 14.31 and A/F = 14.75 in sulfur-free gases is shown in [Figure 6](#).

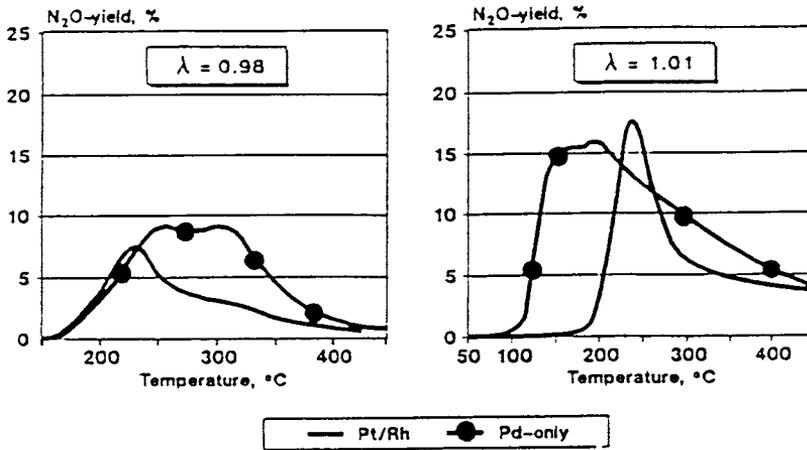


Figure 6: Model Gas Test Results - Comparison of 5Pt/1Rh (40g/ft³) with Pd-only (80g/ft³); Formation of N₂O (SV=50.000h⁻¹, fresh catalyst);

Again, for the Pd-only catalyst a higher overall formation of N₂O, in this case expressed as yield Y

$$Y_{N_2O} = \frac{n_{N_2O, out}}{n_{NO_x, in}} \cdot \frac{1}{2} \quad (n = \text{molar flow of the component}) \quad (2)$$

was determined especially under lean conditions at temperatures below 200°C and under rich conditions at temperatures in the light-off range at about 250 to 350°C. Generally it could be observed in the model gas test, that in the temperature range of catalyst light-off, approx. 10 to 15 % of the NO_x is converted into N₂O. In further experiments it will be checked whether these findings are confirmed under vehicle operation conditions and how dynamic vehicle operation conditions influence the catalyst behaviour.

Summarizing, promising activity improvements could be achieved in model gas experiments with Pd-only catalysts, even though some open questions regarding sulfur poisoning or the formation of secondary emissions have to be answered.

3.2 Physicochemical Characterization

The oxidation state, i.e. the electron density of Pd particles is of significant interest. Recently de Vries et al. have investigated different lanthanum doped automotive catalysts and detected several different Pd species on the catalysts [17-21]. The higher electron density of the Pd particles has an influence on the chemisorption of hydrocarbon species.

The data of Table 2 give some literature reference binding energy values of different Pd species [17].

Table 2: Binding energy values

Pd species	Binding energy [eV]	Full width at half maximum [eV]
Pd metal	334,9	1,1 ^a
Pd black	335,0	1,1-1,5 ^b
Pd	334,8 - 335,1	1,9 ^c
PdO _{1-x}	335,6	1,6
PdO	336,3	2
PdO ₂	337,4-338,3	2,5

^a Pd foil; ^b XPS pass energy 50 eV, values depend on the particle size of the sample;

^c values measured in the presence of La, Zr, etc.

In the present investigation different washcoat systems developed for Pd-catalysts were analyzed by XPS. For catalyst samples described in Table 3 PdO₂ species were not detected, but significant amounts of slightly oxidized Pd at 335,2 to 335,5 electron volts were found. Table 3 shows some results.

Table 3: XPS-binding energies of fresh Pd-only catalysts (full width at half maximum)

Catalyst sample	Binding Energy [eV]	Pd species
CeO ₂ /Al ₂ O ₃	335,0 - 335,2	Pd/PdO _{1-x}
stabilized Al ₂ O ₃	334,9 (1.9) 335,9 (2.0)	Pd/PdO _{1-x}
stabilized Washcoat	334,8 (1.9)	Pd

In all ceria containing catalysts cerium occurs mostly in the reduced oxidation state (Ce-III). CeAlO₃ was also detected.

The existence of a partially oxidized Pd species (PdO_{1-x}) can be assumed for the catalyst sample shown in Figure 7b due to the large width at half maximum of the peaks around 334,9 eV or the shift of the peaks up to 335,6 eV. This type of Pd on the catalyst surface can be interpreted as nonstoichiometric Palladium oxide i.e. PdO_{1-x} and is an efficient catalyst for the hydrocarbon oxidation [22]. After ageing in most of the cases stoichiometric Palladium oxide (PdO) was observed.

Electropositive elements lead to an increase of the surface concentration of Pd and tend to stabilize the dispersion at higher Pd loadings. This is shown in Figure 7a and b by comparing the intensities of the Pd 3d_{3/2} and Pd 3d_{5/2} peaks. The fresh catalyst sample in Figure 7a(stabilized washcoat) shows a lower surface concentration of Pd (0,16%-atom) compared to the catalyst sample shown in Figure 7b (stabilized alumina, 0,93%-atom).

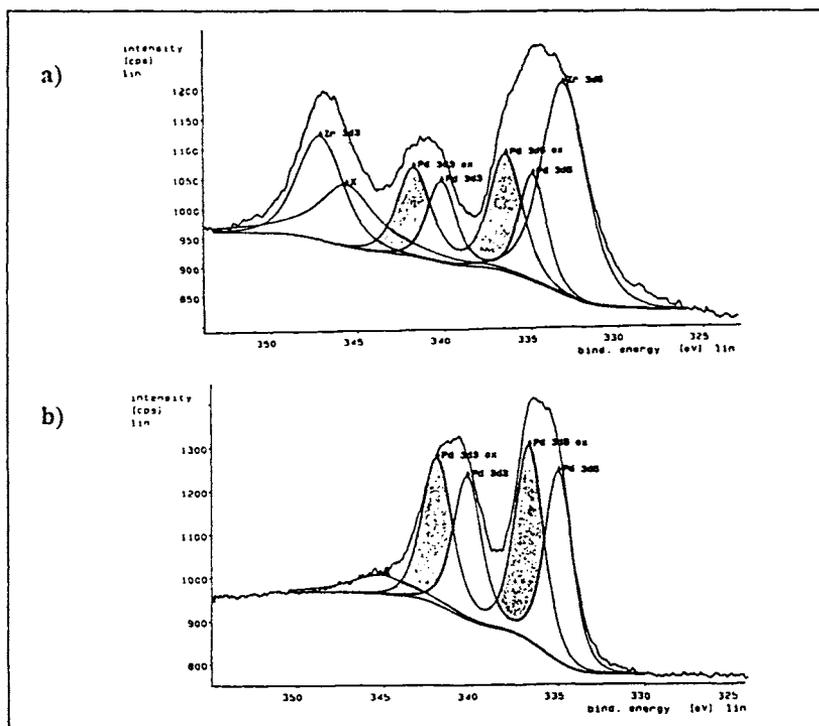


Figure 7: XPS-spectra a) stabilized washcoat
b) stabilized Al_2O_3

3.3 Engine and Vehicle Test Results

3.3.1 Pd-only catalysts

For the experiments described here, the stabilized washcoat system was used for the Pd-only catalysts. First the influence of the Pd-loading on catalyst light-off was investigated under both stoichiometric and lean conditions. The Pd-loading was varied over a very broad range from 3.5 to 40 g/l and the catalyst performance was compared to that of a reference Pt/Rh-catalyst.

Furthermore CO-chemisorption experiments were conducted with the Pd-catalysts. The results are summarized in [Figure 8](#).

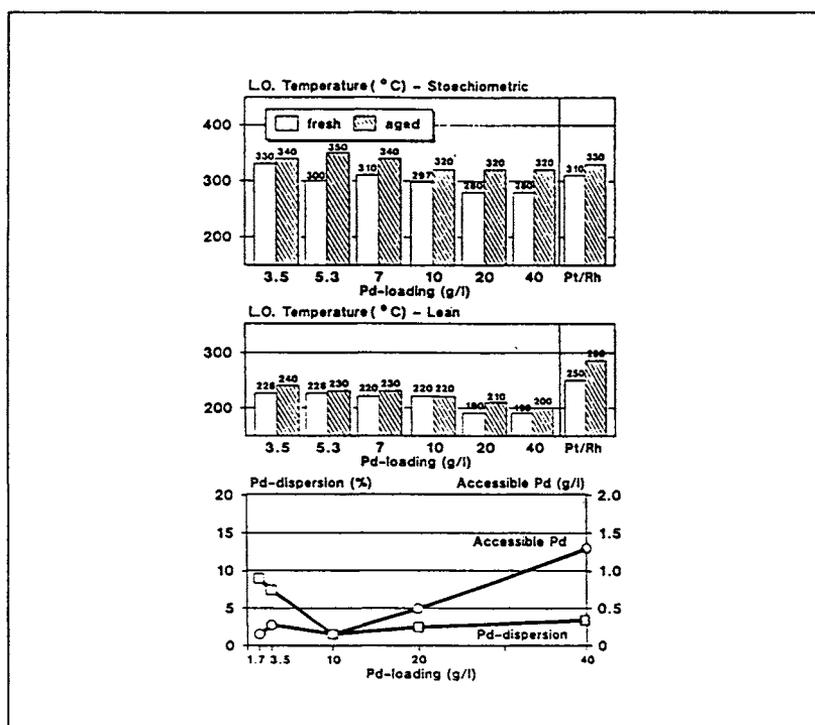


Figure 8: Temperatures for 50 % conversion of HC and Pd-dispersion as a function of the Pd-loading (aging = 100 h, 870 °C, fuel cut method);

For the fresh Pd-only catalysts under stoichiometric conditions a 50°C difference could be observed for the HC-light-off temperature comparing 3.5 to 40 g Pd/l. These differences more or less disappeared after aging and in all cases, i. e. fresh and aged, the Pt/Rh-system ranged in the midfield regarding HC-light off. But this result changed for the lean exhaust gas composition. For Pd-only a much lower light-off temperature was determined as compared to Pt/Rh and in all cases, fresh and aged the influence of an increasing Pd-loading could be observed, most probably due to the higher accessible Pd-surface that is obtained with higher loadings. The Pd-dispersion was nearly constant.

In the following vehicle test study catalysts with a 100 g Pd/ft³ loading were used. For the three different vehicles chosen the ratio of catalyst volume to mass of the vehicle varied from 1.4 liter catalyst/ton vehicle (A) over 2.1 l/t (B) to 2.6 l/t (C). FTP 75 tests were conducted for the fresh and 50 h, 900°C, fuel cut aged systems. The conversion rates for CO, HC and NO_x are given in [Figure 9](#).

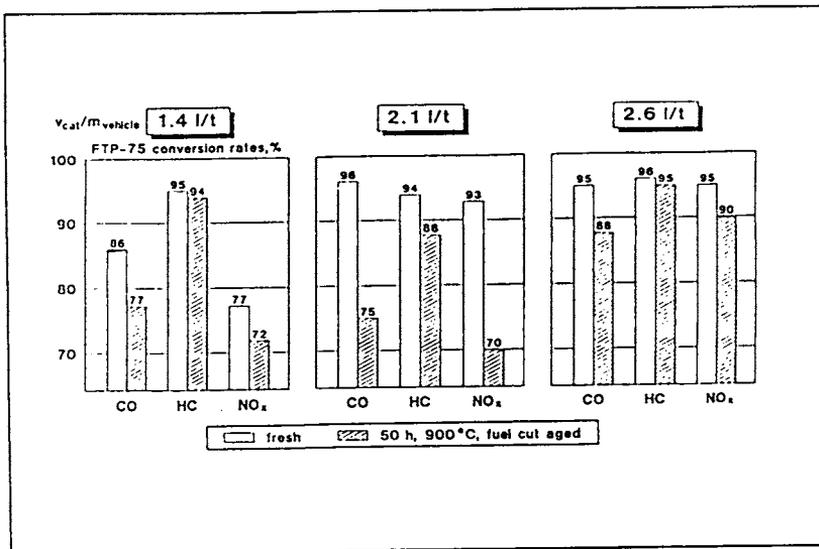


Figure 9: FTP 75 test results for Pd-only catalysts (100 g Pd/ft³)

For the fresh samples especially for the vehicles B and C conversion rates of about 95 % could be achieved for all three components, but only for vehicle C similar activities were maintained after aging.

These results might indicate that for the use of Pd-only technologies in vehicles with tough emission control requirements a higher catalyst volume must be used as compared to Pt/Rh or Pd/Rh converters.

3.3.2 Pd/Rh-Catalysts

In the experiments described below a stabilized washcoat type impregnated with Pd and Rh was compared to an $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ - based Pt/Rh-catalyst. First some engine test results are given in Figure 10.

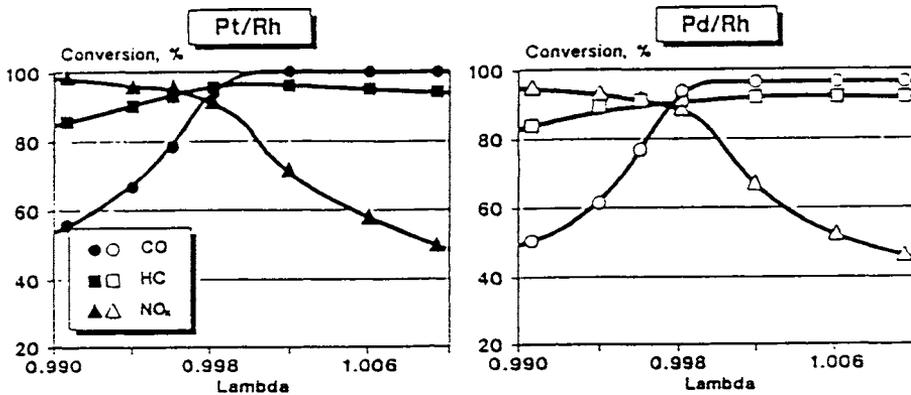


Figure 10: Engine sweep test comparison - Pt/Rh versus Pd/Rh (5/1, 40 g/ft³: 50 h, 930 °C, fuel cut aged; T=450 °C, 1 Hz ± 1 A/F)

Comparing the aged Pd/Rh- with Pt/Rh-systems only little differences were observed, e. g. small deficits regarding NO_x around stoichiometry for Pd/Rh, but this is hardly influencing the A/F-window. Based on this promising data, this Pd/Rh-technology was investigated on different vehicles in different test cycles.

In the vehicle study first the influence of the vehicle's A/F-management on catalyst performance is investigated. The European MVEG-A test cycle was driven, the vehicle had a 6-cylinder 2.8 l engine. Figure 11 shows how a modification of the A/F-management influences exhaust gas temperature and raw emissions (Figure 11a) as well as the catalyst activity (Figure 11b) for Pt/Rh and Pd/Rh.

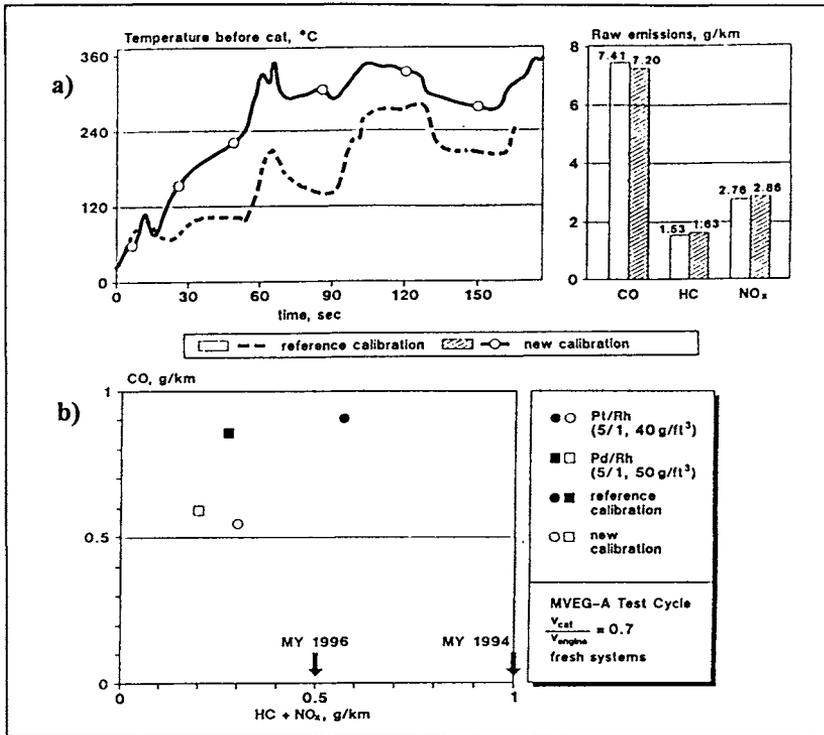


Figure 11: Influence of the A/F-management on a) exhaust gas temperature and raw emission b) catalyst performance (MVEG-A test, $V_{cat}/V_{engine}=0,7$, fresh systems, 5Pt/1Rh, 40 g/ft³, 5Pd/1Rh, 50 g/ft³;))

From Figure 11 a) it becomes clear that the new calibration mainly leads to a steeper temperature increase, whereas the raw emissions are hardly influenced. This gives in general improved emission levels due to a faster catalyst light-off, as shown in Figure 11b). The data clearly demonstrate at least equivalence for the Pt/Rh- and the Pd/Rh-technologies, the modelyear 1996 European standards could easily be met with the cheaper Pd/Rh-system with a relatively small catalyst volume.

Similar conclusions can be drawn from the results shown in Figure 12, where the same Pt/Rh- and Pd/Rh-catalysts were tested on two different vehicles in the MVEG-A and FTP75 test cycle and comparable activities were obtained.

It should be put emphasize on the good CO bag 1 performance during the MVEG-A test cycle and some bag 3 HC advantages for Pd/Rh while the NO_x activity is comparable (see Figure 12a).

During the FTP 75 tests the good aging stability for the Pd/Rh technology especially for CO and NO_x is remarkable [Figure 12b].

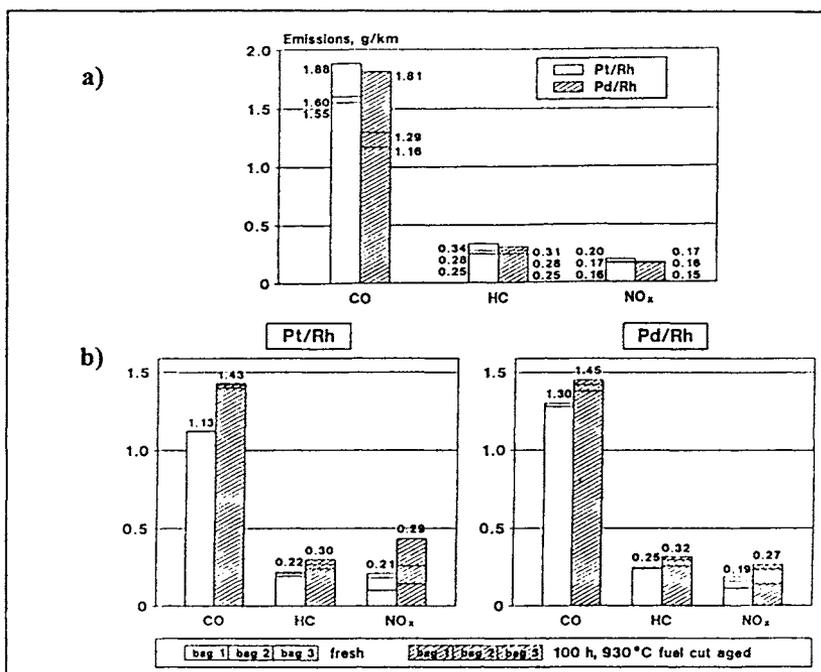


Figure 12: Vehicle test results - 5Pt/1Rh versus 5Pd/1Rh (50 g/ft³)
 a) $V_{cat}/V_{engine}=0.84$, MVEG-A test cycle; 100 h, 930°C fuel cut aged);
 b) $V_{cat}/V_{engine}=1$, FTP75 test cycle; fresh and 100 h, 930°C, fuel cut aged, emissions in g/mile);

Summarizing these findings, Pd/Rh-technologies offer from the technical aspect as well as for cost reasons promising alternatives compared to the more expensive well-known Pt/Rh-technologies. This seems to be true already for vehicles that are approved for the current legislation and still as an outlook for future work, further improvement should be possible by optimizing A/F-management systems and/or the quality of the fuel.

4. CONCLUSIONS

From the experiments the following conclusions can be drawn for the Pd-only catalyst.

- Model gas test results

In SO₂-free gas mixtures new developed Pd-only catalysts performed equal to conventional Pt/Rh-systems. By addition of 200 vppm SO₂ the Pd-only catalyst lost activity. The Pd-only systems formed greater amounts of secondary emissions like NH₃ or N₂O than Pt/Rh-catalysts.

- Results of XPS-experiments

With new developed washcoats an improved Pd-dispersion could be achieved, also a stabilization of slightly oxidized PdO_{1-x} species was observed.

- Vehicle test results

Dependent on the ratio of catalyst volume to mass of the vehicle conversion rates exceeding 90 % for all pollutants were achieved after severe engine aging.

For the Pd/Rh-catalysts the following can be summarized:

- Engine test results

Comparable activities for fresh and aged Pd/Rh- and Pt/Rh-systems could be demonstrated.

- Vehicle test results

Comparing Pd/Rh- with Pt/Rh-technologies on different vehicles in European and FTP 75 - test cycles similar to lower emissions were achieved with the cheaper Pd/Rh-catalysts.

After severe aging model year 1996 legislation for the European Union could be met with Pd/Rh-systems.

5. ACKNOWLEDGEMENT

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