

# Development of high performance, Pd-based, three way catalysts

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## Abstract

The use of Pd in three-way catalytic (TWC) converters of automobiles presents serious limitations which are related to sintering, poisoning and excessive selectivity for HC and CO oxidation, making NO<sub>x</sub> reduction difficult. In the present work, an advanced automotive exhaust catalyst design is applied which reduces, to a large extent, these shortcomings of Pd. This catalyst is based on dispersion of Pd on YSZ (ZrO<sub>2</sub> stabilized with 8 mol-% Y<sub>2</sub>O<sub>3</sub>) forming the internal layer of a three-layer washcoat. The external layers contain small quantities of Pt and Rh dispersed on suitable supports, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and W<sup>6+</sup>-doped TiO<sub>2</sub>, respectively. This scheme offers a high performance TWC with low light-off temperature for the conversion of all three pollutants (CO, HC and NO<sub>x</sub>), enhanced poisoning tolerance and improved thermal resistance.

*Keywords:* Automotive catalyst; Carbon monoxide oxidation; Hydrocarbon oxidation; Nitric oxide reduction; Palladium; YSZ

## 1. Introduction

Stricter automotive emission regulations will be adopted in Europe, USA and Japan, necessitating the application of various strategies to significantly reduce carbon monoxide, hydrocarbon and NO<sub>x</sub> emissions. The only available technology is the catalytic transformation of these pollutants. Thus, catalysts which are active at low temperatures for reduction of cold-start emissions and tolerant to high temperatures, together with a rational use of the rare platinum group metals (PGM) are required. Research efforts are focused on improved converter designs such as warm-up or electrically heated ones and on advanced catalytic technologies.

With respect to the latter, recent investiga-

tions have shown that palladium catalysts possess high efficiency for the oxidation of CO and HC and moderate activity for NO<sub>x</sub> reduction [1,2]. With an accurate air to fuel ratio metering system, Pd-only catalysts are efficient within a narrow operating window, significantly narrower than in the case of conventional Pt–Rh three-way catalysts. Furthermore, Pd presents some serious limitations such as rapid sintering under reducing conditions and poisoning by sulfur at low temperatures, while high Pd loadings can be too selective for HC and CO oxidation, making NO<sub>x</sub> reduction difficult. Current research efforts aim towards eliminating these disadvantages of Pd through advanced catalyst design.

In the present work, the influence of the carrier (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, TiO<sub>2</sub>–W<sup>6+</sup> and YSZ) on the catalytic performance of supported Pd catalysts under CO and C<sub>2</sub>H<sub>4</sub> oxidation and

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NO reduction conditions was investigated. A strong influence of the carrier on the specific activity of Pd (turnover frequency) was observed in all cases. An advanced catalyst design is applied in order to develop a high performance, Pd mainly TWC. This catalyst is based on the dispersion of Pd on YSZ, forming the internal layer of a three-layer monolith wash-coat. The external layers contain small quantities of Pt and Rh dispersed on suitable supports, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and W<sup>6+</sup>-doped TiO<sub>2</sub>, respectively. This scheme gives a high performance TWC with low light-off temperature for the conversion of all three pollutants (CO, HC and NO<sub>x</sub>), enhanced poisoning tolerance and improved thermal resistance.

## 2. Experimental

### 2.1. Catalyst preparation and kinetic measurements

Pd catalysts were prepared by impregnation of the supports with a PdCl<sub>2</sub> solution of appropriate strength so as to yield 0.5 wt.-% metal loading. Five supports were used: SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> (8 mol.-% Y<sub>2</sub>O<sub>3</sub>),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and W<sup>6+</sup>-doped TiO<sub>2</sub>. The latter support was prepared by thermal treatment of TiO<sub>2</sub> and WO<sub>3</sub> at 900°C for 5 h, a procedure which was also followed in the case of undoped TiO<sub>2</sub> (rutile form). The catalysts were reduced under H<sub>2</sub> flow at 400°C for 1 h. They were characterized with respect to exposed metallic area and metal dispersion by selective chemisorption of H<sub>2</sub> at room temperature. Kinetic measurements were carried out in a CSTR-type reactor [3]. Analysis of reactants and products was carried out by on line gas chromatography and IR spectroscopy. Three reactions were studied: CO and C<sub>2</sub>H<sub>4</sub> oxidation and NO reduction by CO in a wide range of reactants partial pressures and temperatures (150–500°C).

In order to examine the effect of metal dispersion and metal crystallite size on turnover

number, a 0.3% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst of approximately 100% dispersion was prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Pd(NO<sub>3</sub>)<sub>2</sub> solution at pH 10 (NH<sub>3</sub>). Lower dispersions, namely 63%, 38%, 24% and 4%, were obtained by calcination of this catalyst in air at 550, 650, 750 and 800°C, respectively, for 2 h.

### 2.2. Preparation and testing of monolithic catalysts

The Pd catalysts were prepared following the procedure which was described above. A thick aqueous suspension of the catalyst was then prepared and the catalyst particle size was reduced by wet milling for 2–3 h. A new suspension was subsequently prepared, using the catalyst of fine particles at a concentration of approximately 30%, at a pH of 3 and a temperature of approximately 40°C. A monolith specimen of cylindrical shape (16 mm diameter by 5 mm length) was immersed in this suspension for 5–10 min. When it was removed from the suspension it was blown with forced air, dried at 110°C for 1 h and calcined at 600°C for 2 h. This procedure was repeated until the desirable loading was achieved. The catalyst loading was determined gravimetrically. The monolith was placed in the reactor where the catalyst was reduced in situ, prior to initiation of the reaction.

## 3. Results and discussion

### 3.1. Kinetic measurements

Kinetic results of C<sub>2</sub>H<sub>4</sub> oxidation over the Pd catalysts employed in the present study are shown in Fig. 1. The influence of oxygen partial pressure, at constant ethylene pressure, on turnover frequency is shown in Fig. 1a, while the influence of ethylene partial pressure at constant oxygen pressure is illustrated in Fig. 1b. In both cases, turnover frequency exhibits a maximum, illustrating the competitive adsorp-

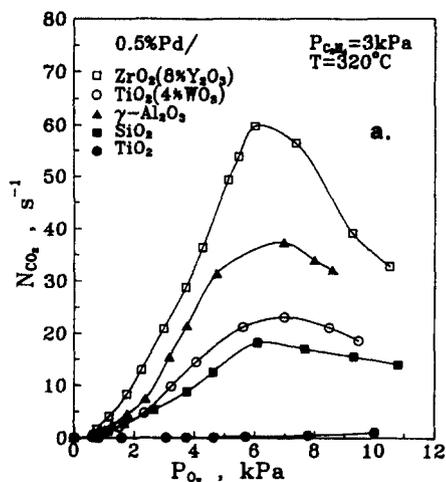


Fig. 1. Activity (turnover frequency) of Pd catalysts supported on different carriers under  $C_2H_4$  oxidation. Effect of  $O_2$  (a) and  $C_2H_4$  (b) partial pressures.

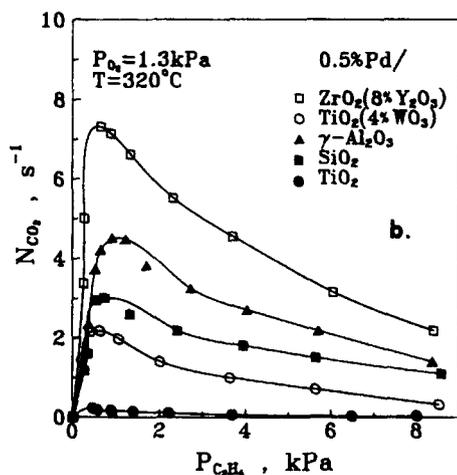


Fig. 1 (continued).

tion process of the two molecules. In Fig. 1b, the maximum occurs at low ethylene pressures and it is very sharp, as compared to that of Fig. 1a, indicating that  $C_2H_4$  is strongly adsorbed on Pd and saturation is achieved very rapidly. The partial pressure at which the maximum occurs is not significantly influenced by the carrier which is employed to disperse the metal, in contrast to the activity itself which seems to be significantly affected by the carrier. Pd-YSZ exhibits the highest activity, while Pd/ $TiO_2$  the lowest activity.

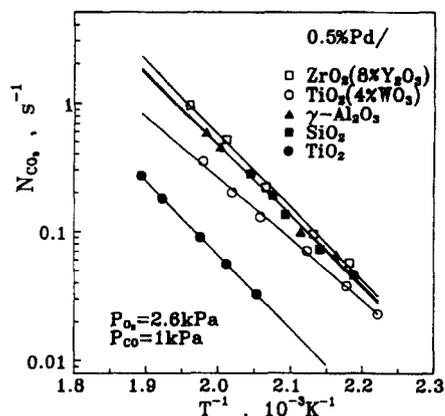


Fig. 2. Influence of temperature on the activity of supported Pd catalysts under CO oxidation.

The influence of the carrier on the catalytic activity of Pd under CO oxidation conditions is illustrated, in the form of an Arrhenius plot, in Fig. 2. The activation energies do not differ significantly, varying within the range of 22 to 26 kcal/mol. Fig. 3 shows the influence of the carrier on turnover frequency in the NO–CO reaction, under variable NO partial pressure. It is apparent that in all cases the specific activity of Pd is highest when it is dispersed on YSZ and it decreases in the order: YSZ >  $\gamma-Al_2O_3$  >  $SiO_2$  >  $TiO_2$  (4%  $WO_3$ ) >  $TiO_2$ . The high activity of Pd-YSZ catalyst may be related to the high oxygen anion mobility of YSZ which may be followed by oxygen spill-over onto the metallic sites [3]. Oxygen spill-over onto the Pd

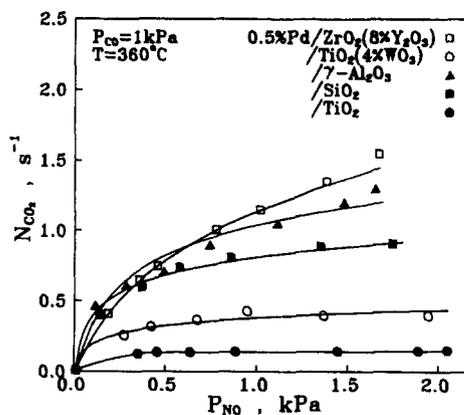


Fig. 3. Activity of supported Pd catalysts under NO reduction by CO. Effect of NO partial pressure.

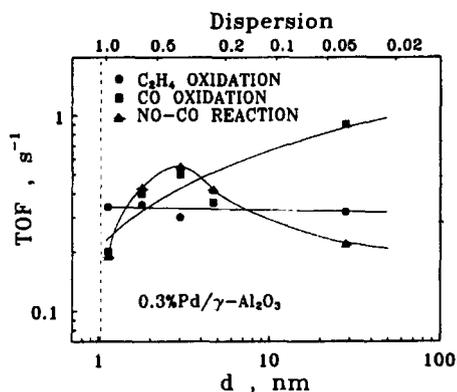


Fig. 4. Effect of metal dispersion and crystallite size of 0.3% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on turnover frequency of C<sub>2</sub>H<sub>4</sub> oxidation ( $P_{C_2H_4} = 1\%$ ,  $P_{O_2} = 1\%$ ,  $T = 250^\circ\text{C}$ ), CO oxidation ( $P_{CO} = 2\%$ ,  $P_{O_2} = 1\%$ ,  $T = 250^\circ\text{C}$ ) and NO reduction by CO ( $P_{CO} = 0.5\%$ ,  $P_{NO} = 0.5\%$ ,  $T = 350^\circ\text{C}$ ).

crystallites causes an enhancement of the work function and, thus, weakening of the Pd–O bond.

The results presented in Fig. 1, Figs. 2 and 3 could be attributed to dispersion effects, if it is assumed that the three reactions are structure sensitive. The dispersion of Pd on the different carriers is different, since, their surface area varies significantly. Based on hydrogen adsorption, the dispersion of Pd was found to be: for YSZ:37%,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:61%, SiO<sub>2</sub>:65%, TiO<sub>2</sub> (4% WO<sub>3</sub>):33% and TiO<sub>2</sub>:33%.

Turnover frequencies of C<sub>2</sub>H<sub>4</sub> and CO oxidation and NO reduction by CO are shown in Fig. 4 as a function of the average Pd crystallite size of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The variation of the dispersion of this catalyst was achieved by sintering of the highly-dispersed formulation at different temperatures for variable period of time. It is apparent that C<sub>2</sub>H<sub>4</sub> oxidation is a facile reaction since its turnover frequency is not at all affected by Pd dispersion, while CO oxidation and NO reduction exhibit a weak dependence on Pd crystallite size. It is important to note that the variation of specific activity with the carrier (Fig. 1, Figs. 2 and 3) can not be explained by structure sensitivity considerations and should be attributed to interactions between the metal crystallites and the carrier.

### 3.2. Performance of Pd-based, monolithic converter

Pd-YSZ slurries were applied to monolithic structures and then external layers of Rh/TiO<sub>2</sub> (W<sup>6+</sup>) and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were deposited. All carriers had been promoted with 6% CeO<sub>2</sub> and 2% La<sub>2</sub>O<sub>3</sub>. With this type of geometric configuration, Pd is protected from poisoning and alloy formation with Pt, and Rh is also protected from poisoning and undesirable interactions with Al<sub>2</sub>O<sub>3</sub> at high temperatures. The use of YSZ as a carrier for Pd and TiO<sub>2</sub> (W<sup>6+</sup>) for Rh, has been found [3] to improve their activity, giving a TWC of higher activity, as compared to the conventional one.

Light-off temperatures of a 3-layer catalyst containing Pt, Rh and Pd are shown in Fig. 5 for TW operation, and are compared with a conventional catalyst in which the same quantity of noble metals are uniformly distributed within the washcoat of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (both catalysts contain 0.034% Pt, 0.0086% Rh, 0.039% Pd). It is apparent that the 3-layer catalyst exhibits higher activity for all three reactions since the light-off temperature is lower in all cases. The beneficial effect of the addition of the Pd-YSZ component is also illustrated in Fig. 5 by comparison of the

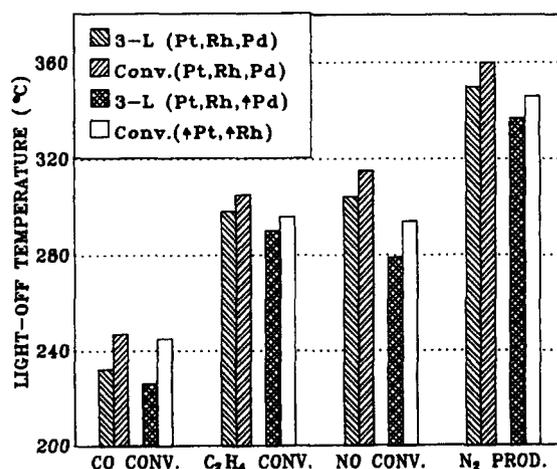


Fig. 5. Comparative results of light-off temperature of 3-layer catalysts of different noble metal content and of conventional TWCs at the stoichiometric point of operation.

performance of a 3-layer catalyst which contains Pd (0.031% Pt, 0.0085% Rh, 0.073% Pd) with that of a conventional one which does not contain Pd (0.070% Pt, 0.014% Rh). The conventional catalyst contains almost twice the amount of Pt and Rh as compared to the 3-layered one while the latter contains an amount of Pd equal twice that of Pt. It is apparent that the Pd-based catalyst exhibits significantly higher activity, even for NO reduction which is the most difficult reaction on Pd. The enhancement of activity is due to the higher activity of the Pd-YSZ combination and the inherently higher activity of the 3-layer geometric configuration.

#### 4. Conclusions

The catalytic activity of Pd under reactions of automotive exhaust emissions treatment (CO and C<sub>2</sub>H<sub>4</sub> oxidation and NO reduction) can be altered significantly using different supports. The use of Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> carrier instead of the conventional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> improves significantly the activity of Pd. This may be due to

oxygen spillover from the support to the catalyst sites. The promotional effect of the support on the activity of Pd is not related to metal dispersion or, equivalently, to metal crystallite size.

A monolithic catalyst for TW operation, based on the dispersion of Pd on YSZ, forming the internal layer of a three-layer washcoat, was developed. The external layers contain small quantities of Pt and Rh dispersed on suitable supports,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and W<sup>6+</sup>-doped TiO<sub>2</sub>, respectively. This configuration gives a high performance TWC with lower light-off temperature for the conversion of all three pollutants (CO, HC and NO<sub>x</sub>) as compared to conventional TWC. Because Pd is protected from poisoning and alloy formation with Pt, this catalyst may also exhibit enhanced poisoning tolerance and improved thermal resistance.

#### References

- [1] J. Detting, Z. Hu, Y.K. Lui, R. Smaling, C.Z. Wan and A. Punke, *Stud. Surf. Sci. Catal.*, 96 (1995) 461–472.
- [2] J.C. Summers and W.B. Williamson, *ACS Symp. Ser.* 552 (1994).
- [3] I.V. Yentekakis, C.A. Pliangos, V.G. Papadakis, X.E. Verykios and C.G. Vayenas, *Stud. Surf. Sci. Catal.*, 96 (1995) 375–385.