

## Durability of three-way platinum and rhodium catalysts in oxidising, reducing and cycled environments

J.A. Botas, R. Ferret, M.A. Gutiérrez-Ortiz  
and J.R. González-Velasco

*Departamento de Ingeniería Química, Facultad de Ciencias, Universidad del País Vasco,  
Euskal Herriko Unibertsitatea, P.O. Box 644, 48080 Bilbao, Spain*

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\* Correspondence and reprints.

### RÉSUMÉ

Le comportement catalytique (conversions de CO, HC et NO, et température d'ignition) de catalyseurs trois-voies MN/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (MN: Pt, Rh, Pt-Rh) **fraîs** et **vieillis** sous sévère conditions en **environnement** oxydant, **réducteur** et cyclique, a **été** analysé. **Les résultats** obtenus indiquent que **parmi les** catalyseurs étudiés, le bi-métallique Pt-Rh est le plus **actif**.

Mots **clés** : TWC, catalyseur trois-voies, vieillissement **thermique**, température d'ignition.

### ABSTRACT

The three-way catalytic **behaviour** (CO, HC and NO, conversions and light-off temperatures) of MN/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (MN: Pt, Rh, Pt-Rh) catalysts, fresh and aged under severe oxidizing, reducing and cycled environments, has been analyzed. The bimetallic Pt-Rh catalyst resulted the most active among those tested.

Keywords : **TWC**, three-way catalyst, thermal aging, light-off temperature.

### 1. INTRODUCTION

The simultaneous reduction of carbon monoxide, nitrogen oxides, and unburned hydrocarbons in the automobile exhaust gases at lowest temperatures is the main task of the three-way catalysts (TWC). Due to the **stricter** standard limits for such emissions, new catalytic systems more efficient and durable should be developed.

## 2. EXPERIMENTAL

### 2.1. Catalysts

The alumina used as support was SAS-1/16 supplied by La Roche Chemicals with a particle size between 0.5 and 1.0 mm. To be stabilised it was calcined under air at 700°C for 4 hours previously to subsequent treatments. The incorporation of cerium was made by the incipient wetness from a  $\text{Ce}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  solution, and final incorporation of platinum *or/and* rhodium by adsorption from  $\text{H}_2\text{PtCl}_6 \cdot n\text{H}_2\text{O}$  *or/and*  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  solutions. The detailed preparation method has been reported previously [1,2]. The composition of the prepared catalysts is presented in Table I.

Table I. Composition of the prepared catalysts, wt.-%

Catalyst	CeO <sub>2</sub> , wt.-%	Pt, wt.-%	Rh, %-wt
Pt monometallic	8.83	0.079	—
Rh monometallic	8.84	—	0.021
Pt-Rh bimetallic	9.16	0.081	0.021

### 2.2. Aging procedure

The catalysts were submitted to severe accelerated aging at 900°C for 5 hours under the oxidising and reducing environments shown in Table II, with a space velocity of 125000 h<sup>-1</sup>, and subsequent cooling down to initial reaction temperature. The cycled treatment corresponds to alternate cycles between oxidising and reducing streams with a frequency of 0.017 Hz (30 seconds each).

Table II. Composition of the aging feedstreams

Environment	CO, vol.-%	O <sub>2</sub> , vol.-%	H <sub>2</sub> O, vol.-%	N <sub>2</sub> , vol.-%
Oxidising (OE)	—	2.5	10.0	to balance
Reducing (RE)	5.0	—	10.0	to balance
Cycled (CE)	—	2.5	10.0	to balance
	5.0	—	10.0	to balance

### 2.3. Activity tests

Catalytic activity data were obtained by using a conventional fixed-bed reactor at atmospheric pressure as described elsewhere [1,2], using 3.5 cm<sup>3</sup> (ca. 1.8 g) of

catalyst. The experiments were made—trying to simulate the closed-loop emission control system in the **automobile**— under cycling the two following **feedstreams** prepared in two independent gas blending systems, with a frequency of 1 Hz, an amplitude of  $\pm 0.5$  A/F, and a space velocity of  $125000 \text{ h}^{-1}$  (STP):

**Reducing feedstream** (air-to-fuel ratio = 14.13). It was composed of 10%  $\text{CO}_2$ , 1.60% CO, 900 ppm NO, 900 ppm  $\text{C}_3\text{H}_6$ , 0.465%  $\text{O}_2$ , 10.0%  $\text{H}_2\text{O}$ , and a balance of  $\text{N}_2$ .

**Oxidising feedstream** (air-to-fuel ratio = 15.17). It consisted of 10%  $\text{CO}_2$ , 0.40% CO, 900 ppm NO, 900 ppm  $\text{C}_3\text{H}_6$ , 1.26%  $\text{O}_2$ , **10.0%  $\text{H}_2\text{O}$** , and a balance of  $\text{N}_2$ .

The temperature was increased from 100 to  $600^\circ\text{C}$  at a rate of  $30\text{C min}^{-1}$ , and the conversion data were continuously measured by non dispersive infrared ( $\text{CO}$  and  $\text{CO}_2$ ), flame ionisation (HC), magnetic susceptibility ( $\text{O}_2$ ), and **chemiluminescence** ( $\text{NO}_x$ ).

### 3. RESULTS AND DISCUSSION

The thermal treatments at high temperature modify the textural characteristics of the **ceria-doped** alumina as shown in Table III. A decrease of the BET surface area with the aging can be observed: fresh (100%) > OE (70%) > RE (69%) > CE (58%). The pore volume is consequently reduced and the pore size increased. The small metal content did not affect practically the physical structure of the catalysts.

Table III. Textural properties of  $\text{CeO}_2/\text{Al}_2\text{O}_3$

	Fresh	OE	RE	CE
$S_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$	176.3	122.6	122.3	102.7
$V_p, \text{cm}^3 \cdot \text{g}^{-1}$	0.835	0.763	0.766	0.736
$r_p$ (average), nm	9.48	12.45	12.54	14.35
$r_p$ (mode), nm	6.12	8.65	8.65	8.65

Figure 1 shows, as an example, the light-off curves corresponding to the Pt-Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$  catalyst, fresh and aged. Similar curves were obtained for every catalyst and pollutant. From these temperature-programmed conversion profiles, the

light-off temperature which is necessary to achieve 50% conversion,  $T_{50}$ , and the stationary conversion at the normal running temperature of 500°C,  $X_{500}$ , were determined for every component, resulting in the values shown in Table IV.

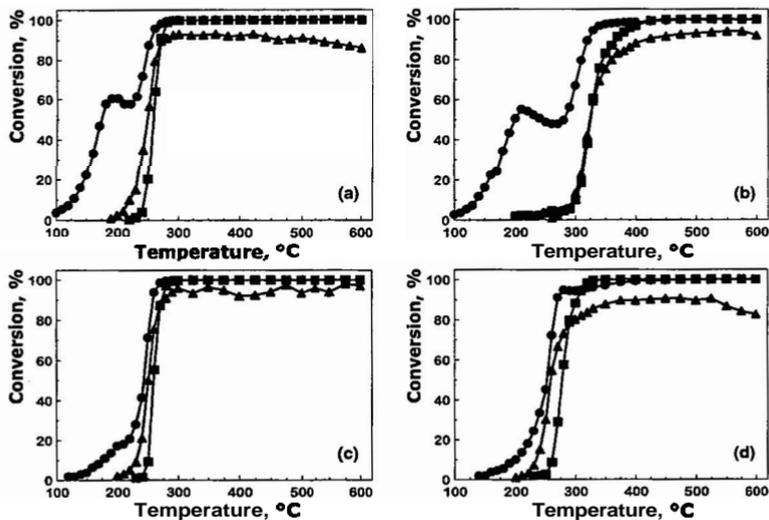


Figure 1. Three-way conversions for the Pt-Rh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, fresh (a), OE (b), RE (c), CE (d). (●: CO; ▲: NO; ■: C<sub>3</sub>H<sub>6</sub>)

The effect of hydrothermal aging on the ceria surface area and on oxygen storage capacity of commercial Pt-Rh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts has been studied by XPS [3] and TPR [4] experiments, concluding that aging the catalyst causes a loss of oxygen storage capacity due to increasing the mean CeO<sub>2</sub> diameter and consequent sintering of the ceria particle which reduces the ceria/noble metal interaction and does not allow the Ce to cycle between oxidation states. This loss of ceria/noble metal contact area due to sintering of particle ceria as well as the sintering of the noble metal particle [3,5] should be responsible of the activity changes observed in Table IV.

Table IV. Catalytic behaviour of the fresh and aged catalysts

Treatment	Pollutant	Light-off temperature, $T_{50}$ (°C)			Conversion, $X_{500}$ (%)		
		Pt	Rh	Pt-Rh	Pt	Rh	Pt-Rh
Fresh	CO	255*	245	173	100	98.7	100
	NO	306	253	247	90.0	71.0	91.0
	C <sub>3</sub> H <sub>6</sub>	300	268	257	100	99.9	100
OE	CO	301*	401	281*	98.3	82.0	99.8
	NO	376	496	325	76.5	53.0	93.0
	C <sub>3</sub> H <sub>6</sub>	343	477	325	99.8	69.8	100
RE	CO	303	256	243	100	100	100
	NO	318	260	250	74.0	79.0	93.5
	C <sub>3</sub> H <sub>6</sub>	316	273	259	100	100	100
CE	CO	290	313	252	99.8	97.4	99.8
	NO	379	318	258	72.0	74.5	89.5
	C <sub>3</sub> H <sub>6</sub>	338	353	277	100	99.8	100

(\*) With these catalysts the CO oxidation occurs in two steps, corresponding to direct oxidation (below 200°C) and WGS and CO+NO reactions (above 250°C), as previously reported [1,2]. For this situation the light-off temperature reported in Table IV has been that corresponding to the last step, i.e. the highest one.

With the monometallic Pt catalyst the CO and C<sub>3</sub>H<sub>6</sub> conversions at 500°C resulted practically invariable; however, a decrease in the NO conversion about **25%** was observed, whether oxidising, reducing or cycled aging. The light-off temperature of NO and C<sub>3</sub>H<sub>6</sub> were increased about 70 and 40 degrees, respectively, for the catalyst aged under oxidising and cycled flow, but much moderate deactivation, about 12 degrees, when aged under reducing conditions. The increase of the light-off temperature for CO, about **40°C**, was independent of the aging environment.

The **monometallic** Rh catalysts aged at high temperatures under oxidising environment suffer from notable deactivation due to the severe sinterization of metal particles [6]. However, it is known that the **sinterized** particles under oxidising atmosphere can be **redispersed** when **exposed** again to reducing streams at high temperatures [7]. This explains the changes in conversions at **500°C** as well as in the light-off temperatures shown in Table IV for the Rh catalyst; better results have been achieved under reducing or cycled than under oxidising environments.

The bimetallic Pt-Rh catalyst remains highly active for the CO/NO/C<sub>3</sub>H<sub>6</sub> conversions even after exposed to any hydrothermal treatment. Also the light-off temperatures of the Pt-Rh resulted not so high as those of the individual Pt and Rh and closer to those of the fresh catalyst. This synergic effect between Pt and Rh had been already stated for fresh catalysts [1]. Recently, Hu *et al.* [8] used **AEM, XPS,** and XRD to characterize catalyst structural changes and establish a correlation between catalyst performance and structure. Pt and Rh in the bimetallic catalyst follow deactivation the same as that for individual phases in the simulated aging process. However, Rh in the aged Pt-Rh catalyst can regenerate in exhaust at low temperature (300°C) due to H<sub>2</sub>/CO spillover on Pt particles which facilitate the regeneration of the inert Rh-aluminate species to Rh metal particles.

As final conclusion, the bimetallic **Pt-Rh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>** has resulted the most active formulation for three-way conversion of CO/NO/C<sub>3</sub>H<sub>6</sub>. Figure I shows the temperature-programmed conversion curves for this optimal formulation, fresh and after aging.

#### ACKNOWLEDGMENTS

The authors **acknowledge** the **financial** support from the Spanish Government (AMB93-574) and the University of the Basque Country (EB076/94).

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