

# Influence of Oxygen on the Performance of a Three-Way Catalyst

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During experiments designed to simulate the oscillations of composition observed upon the catalyst in a vehicle exhaust device, a Pt–Rh bimetallic catalyst supported on alumina was studied for three-way catalytic reactions under both stationary and cycling conditions. The results were compared with those obtained from employing platinum or rhodium metals supported separately upon alumina and indicated that during the operation of the oscillatory regime on the bimetallic catalyst there is a deactivation/activation mode associated with a fast redox process of the rhodium component which becomes partially oxidised to its inactive form, Rh<sub>2</sub>O<sub>3</sub>. Deactivation was not observed with platinum alone nor under steady feed conditions in the bimetallic case. The effect of this cycling deactivation is examined with respect to the temperature required to affect the bulk of the metals, its consequential reorganization of the surface, and subsequent interaction with the oxygen. © 1995 Academic Press, Inc.

## 1. INTRODUCTION

Since their development in the 1970s, catalytic converters have gained both great support and promotion from environmental protection groups. The extent of their influence is reflected in the adoption of this technology by automobile manufacturers throughout the world who now perceive as standard the necessity to reduce toxic exhaust emissions (1). From within the exhaust gas mixture, the hydrocarbon and the carbon monoxide are oxidised into CO<sub>2</sub> and H<sub>2</sub>O, while NO<sub>x</sub> is reduced to nitrogen. The noble metal platinum in association with rhodium is able to perform these parallel reactions when the air/fuel ratio is balanced around the stoichiometric composition (2).

Many studies have been devoted to this subject covering a wide variety of activities (3, 4). Indeed, surface science work has shone new light upon the role of each metal (5–7) while kinetics and reactivity studies have conveyed information about all the reactions which take place within a catalytic exhaust device (8). This has included the discovery that the reaction between CO and O<sub>2</sub> is

structure insensitive upon rhodium while important effects of particle size have been observed for the reaction between CO and NO (9). Also, the interactions between Pt and Rh were shown (10) and surface rhodium enrichments were postulated under oxidising conditions. Recently in our laboratory it was confirmed by EXAFS that when a catalyst was submitted to such conditions at relatively high temperature (>600°C) a bulk alloy was formed (11). However, in general these studies are not representative of the *in situ* processes, as three-way converter catalysts never operate under steady-state conditions; the temperature rises very rapidly and particularly, the gas composition undergoes notable fluctuations. The latter results mainly from two types of phenomena. Slow oscillations are due to the acceleration and deceleration phases when the exhaust emissions become either very reducing or very oxidising. Alternatively, the exhaust sensor, usually a ZrO<sub>2</sub> probe, used to detect any oxygen imbalance, induces fast oscillations (i.e., 0.5 to 4 Hz) of the air/fuel ratio about the stoichiometric point (12). A recent publication by Beck and Carr (13) has proved very interesting, as they have studied the effect of aging at high temperature (between 600 and 900°C) on Rh/Al<sub>2</sub>O<sub>3</sub> in an environment which alternates between oxidising and reducing compositions. This work might be correlated with the same type of study undertaken a few years earlier on platinum (14). However, the low frequencies of operation when compared with that of an engine and a simplified gas mixture (oxygen or hydrogen diluted into nitrogen), must be taken into account.

In this paper, we have ascertained the role of platinum and rhodium in a bimetallic catalyst and tried to determine the properties of each metal by comparing the characteristics of the monometallic systems. Particular attention is given to the study of activity under experimental conditions close to those observed in an engine employing a closed-loop emission control system, incorporating representative gas compositions oscillating around the stoichiometric point with high frequencies. We report here not only the role of the catalyst in the chemical conversion processes but also a study of the redox phenomena oc-

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curing in the metallic phase itself, particularly under relatively mild conditions corresponding, for instance, to the warm-up period.

## 2. EXPERIMENTAL

### 1. Preparation and Characterisation of Catalysts

The monometallic and bimetallic catalysts were prepared by the Institut Français du Pétrole (Pt and Pt-Rh) or in our laboratory (Rh) by impregnation of a  $\gamma$ -alumina ( $100 \text{ m}^2 \cdot \text{g}^{-1}$ ) in pellets of 2 to 4 mm in diameter. The precursor salts were  $\text{H}_2\text{PtCl}_6$  and  $\text{RhCl}_3$ , and the coimpregnation method was employed to prepare the bimetallic. After evaporation and drying, the catalysts were calcined in air at 623 K for 4 h and then reduced under hydrogen at 773 K for 8 h. They were then crushed and sieved. The fraction of 80–250  $\mu\text{m}$  was retained for the experiments. The metal loadings are reported in Table 1 ( $M_t$  signifies total metal).

**CO chemisorption.** The apparent  $\text{CO}/M_t$  ratio listed in Table 1 was measured using CO chemisorption at 25°C. An aliquot of 0.100 g of catalyst was reduced under pure hydrogen at 400°C for 1 h and then flushed with purified helium at the same temperature for an additional hour before being cooled to 25°C. The CO was then introduced in pulses of 0.0037  $\text{cm}^3$  until the surface was saturated. The calculations were made with the assumption of  $\text{CO}/M_t = 1$  in the case of platinum and of 1.5 for the rhodium. This latter high ratio has already been observed by several authors who reported it as size dependent (15, 16). This remains plausible since it has been confirmed by infrared studies that CO forms both  $\text{Rh}(\text{CO})_2$  and  $\text{Rh}(\text{CO})$  and that the former tends to increase at the expense of the latter when the particle size decreases (17, 18).

### 2. Catalytic Test Procedure

The catalytic testing equipment was developed in our laboratory by Weibel (19), based upon ideas from Schlatter *et al.* (20). This apparatus is fully driven by computer to simulate the real working conditions of an automotive exhaust.

Three types of experiments can be carried out on the catalytic bed, as detailed in the following paragraphs.

TABLE 1  
Characterisation of Catalysts

Catalyst	%Pt w/w	%Rh w/w	$\text{CO}/M_t^a$
Pt/ $\text{Al}_2\text{O}_3$	1.0	—	0.70
Rh/ $\text{Al}_2\text{O}_3$	—	1.0	0.26
Pt-Rh/ $\text{Al}_2\text{O}_3$	1.0	0.2	1.27

<sup>a</sup> Number of moles of CO/number of moles of metal.

TABLE 2

Reactant Composition<sup>a</sup> and Test Conditions for Steady State and Oscillating Experiments

Test	$[\text{O}_2]$	$[\text{CO}]$	$[\text{NO}]$	$[\text{C}_3\text{H}_8]$	$S_N$	Conditions
A	2960	8910	2050	880	0.45	ss <sup>b</sup>
B	6180	5630	2050	880	1	ss
C	8040	3730	2050	880	1.45	ss
D	5680	6130	2050	880	0.9	osc <sup>c</sup>
	6640	5160	2050	880	1.1	osc
E	2200	9680	2050	880	0.35	osc
	3650	8210	2050	880	0.55	osc
F	7670	4090	2050	880	1.35	osc
	8390	3370	2050	880	1.55	osc

<sup>a</sup> Compositions are given in ppm  $\pm$  1%.

<sup>b</sup> Steady-state.

<sup>c</sup> Oscillating about the mean value ( $f = 0.05, 1, \text{ and } 2 \text{ Hz}$ ).

(i) *Steady-state experiments.* The composition of the reactant mixture is maintained constant throughout the catalytic test. The flow rate was  $200 \text{ cm}^3 \cdot \text{min}^{-1}$ . The temperature of the furnace was increased linearly ( $4^\circ\text{C}/\text{min}$ ) to 550°C. Each experiment was repeated; after this treatment no deactivation was observed; hence the results were given from the second run. This test was used as a reference for all the reactions in a complete gas mixture (i.e., CO, NO,  $\text{C}_3\text{H}_8$ , and  $\text{O}_2$  with  $\text{N}_2$  as the eluant) or using a binary mixture ( $\text{CO} + \text{O}_2$ ,  $\text{NO} + \text{CO}$ , and  $\text{NO} + \text{HC}$ , with  $\text{N}_2$  as the eluant). All the reactions studied along with their compositions are reported in Table 2.

(ii) *Oscillating experiments.* In the test, the reactant composition oscillates between two values at a frequency chosen by the operator, while the temperature is increased linearly. These oscillations are set around a value called  $S_N$  which represents the ratio between oxidising and reducing reactants and which is defined as

$$S_N = \{2[\text{O}_2] + [\text{NO}]/\{\text{CO} + 10[\text{C}_3\text{H}_8]\}.$$

Therefore, when  $S_N$  is equal to unity the reacting medium is stoichiometric; when  $S_N$  is lower or greater than unity the reaction is carried out under reducing or oxidising conditions, respectively. Another important parameter is the amplitude around  $S_N$  which was usually 0.1. Hence, the working conditions are indicated as, e.g.,  $S_N = 1 \pm 0.1$  which means that the extreme compositions are 0.9 and 1.1. Special precautions are taken to equilibrate the flow rates and the pressures in both ramps.

Typically, frequencies between 0.05 and 2 Hz were used, corresponding to periods of 20 and 0.5 s, respec-

tively, which are representative of the fast oscillations occurring in an engine possessing the A/F regulating system ( $ZrO_2$  probe). Nevertheless, for the high frequency of 2 Hz the back-mixing of the two compositions is such that the gas mixture passing through the catalytic bed is similar to that of a steady-state experiment. The amplitude and the form of the oscillations were measured by an oscilloscope connected to a thermocouple detector (TCD) placed directly into the catalytic bed. In this way, it was shown that for frequencies lower than 0.05 Hz a square-shaped signal is observed and that the amplitude of this step decreased linearly until a straight line representative of a steady-state composition was obtained for a frequency of 2 Hz. As in the steady-state experiments, the tests were repeated several times and the results remained constant even after several runs. The compositions and the corresponding  $S_N$  as well as the frequencies and amplitudes are reported in Table 2.

For the two series of tests described above, the results are given in terms of  $T_{50}$  (the temperature at which 50% of a reactant has been converted). They were also verified in the region of 15–25% of conversion and the sequence of activities was proved identical to those observed at 50% of conversion. Therefore, it seems clear that all the catalytic tests were carried out in the chemical regime and that all limitations due to heat or mass transfer were excluded.

(iii) *Step-change experiments.* When a perturbation is applied to a system having a stationary state, then the system will eventually obtain a new stationary state. The transient response of such a system reflects the nature of the steps which drive the reaction and also the kinetics of the reaction. The so-called step-change, or perturbation method, allows the transient response to a step-change in composition to be studied (21).

Two tests were made, using a simplified gas mixture (i.e., only CO or  $O_2$  in the gas stream,  $N_2$  being the diluent): the first was oxidation of adsorbed CO by  $O_2$ , called the oxidation test, and the second a reduction of adsorbed  $O_2$  by CO, called the reduction test.

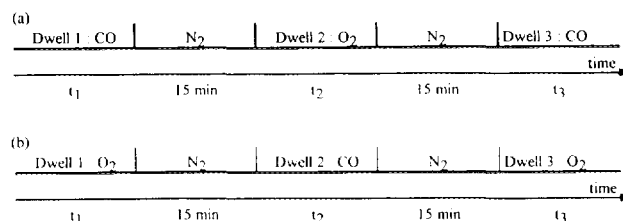


FIG. 1. Scheme of the experimental step-change procedure: (a) oxidation reaction and (b) reduction reaction.

The catalyst (0.40 g) had been stabilised for 1 h under the reducing stream when the oxidation test was carried out (i.e., CO oxidation), and alternatively under the oxidising stream before the reduction (i.e.,  $O_2$  reduction). After this pretreatment the catalyst was flushed with nitrogen for 15 min to remove the gas phase and any weakly adsorbed species. The gas stream was then changed abruptly to that corresponding to the reaction being studied and the system was held for a chosen length of time (dwell 1). The reactor was then purged with nitrogen before switching to the second gas (dwell 2). The transient response to the step-changes was measured by monitoring the evolution of  $CO_2$  from the surface of the catalyst; both area and peak baseline are relevant parameters for study. A summary of the experimental procedure is given in Fig. 1. The design of the apparatus makes the response time to a change in composition not instantaneous; a control experiment performed without a catalyst revealed that the time necessary to purge the system and then reach the theoretical concentration is 1 min. This time interval has been systematically subtracted from the observed value in order to yield more accurate results.

### 3. RESULTS

#### 1. Activity of the Bimetallic Catalyst

*Influence of the catalyst mass.* The first task was the monitoring of the variation of the conversion of CO, NO, and hydrocarbon (HC) on the Pt–Rh/ $Al_2O_3$  catalyst as a

TABLE 3  
Effect of Catalyst Mass on Conversion of CO, NO, and Hydrocarbon on Pt–Rh/ $Al_2O_3$

Gas converted	Conversion, expressed as $T_{50}^a$ (°C), for different masses of catalyst ( $m$ )			
	$m = 50$ mg	$m = 100$ mg	$m = 200$ mg	$m = 300$ mg
CO	249	233	245	239
NO	345	299	300	342
HC	324	283	323	334

<sup>a</sup>  $T_{50}$  is the temperature at which 50% of the reactant has been converted.

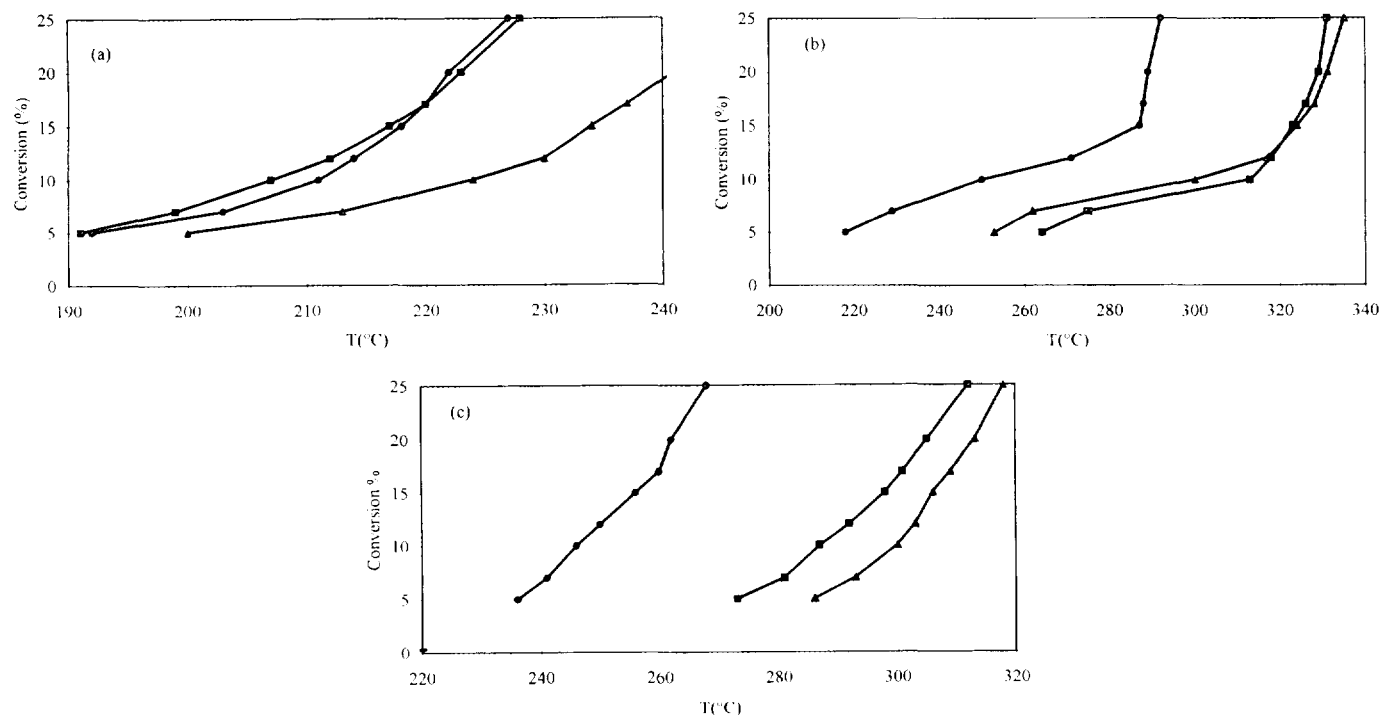


FIG. 2. Activity at low conversion for the three reactants and for different masses of catalyst (●) 100, (▲) 200, and (■) 300 mg; (a) CO, (b) NO, and (c) HC under oscillating conditions with a frequency of 0.05 Hz.

function of mass when oscillating about the stoichiometric point at 0.05 Hz. The results reported in Table 3 proved surprising since above a catalytic mass of 50 mg, no correlation was observed between mass and conversion throughout all the range studied (i.e., 5 to 25%) as shown in Figs. 2a–2b. The efficient conversion of the three pollutants using a catalytic mass of 100 mg is often better than but never less than equivalent to the results employing a catalytic mass of 300 mg. An investigation into this phenomenon was carried out by a systematic study of all the parameters influencing these reactions.

**Influence of the reacting mixture.** The influence of the strength of the reacting medium was studied for three sets of frequencies, i.e., 0.05, 1, and 2 Hz. The compositions were chosen in order to have a very reducing or a very oxidising composition ( $S_N = 0.45$  and 1.45, respectively) and the results were compared with those obtained when oscillating about stoichiometry ( $S_N = 1$ ). The temperatures of half-conversions are reported in Table 4. For comparison, the results at 2 Hz are also given in this table. The results imply that in reducing media, the reduction of NO is very efficient while the oxidation reactions of CO and HC are much less so. These results were somewhat anticipated; however, more surprising was the fact that both oxidation reactions are strongly disfavoured in oxidising media when compared to stoichiometry up to a frequency of 1 Hz. For 2 Hz, i.e., when the conditions

are equivalent to those of the stationary regime, this effect is not observed. This will be confirmed in the following section. Another point to note here is that the conversion of NO is suppressed when operating with  $S_N = 1.45$ , whatever the frequency.

TABLE 4

Conversion Data Expressed as  $T_{50}$  (°C) for 100 mg of Pt–Rh/ $Al_2O_3$  in an Oscillating Regime

	$S_N = 0.45$	$S_N = 1$	$S_N = 1.45$
$f = 0.05$ Hz			
CO	250	233	245
NO	270	299	—
HC	550	283	328
$f = 1$ Hz			
CO	268	228	239
NO	277	310	—
HC	568	300	345
$f = 2$ Hz			
CO	nm <sup>a</sup>	229	202
NO	nm	297	—
HC	nm	286	325
Steady state			
	$S_N = 0.45$	$S_N = 1$	$S_N = 1.45$
CO	251	229	217
NO	260	297	—
HC	29% <sup>b</sup>	289	311

<sup>a</sup> Not measured.

<sup>b</sup> Maximum conversion reached.

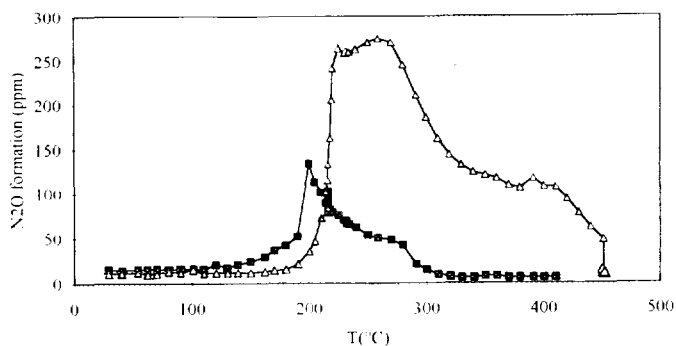


FIG. 3. Conversion under  $N_2O$  on 100 mg of Rh and Pt-Rh supported on alumina under steady-state conditions, ( $\Delta$ ) Rh/ $Al_2O_3$ , ( $\blacksquare$ ) Pt-Rh/ $Al_2O_3$ .

*Comparison with steady-state values.* Another important parameter to be taken into account was the value obtained when operating under steady-state conditions. These data are shown in Table 4. The main result obtained from this set of experiments concerns the CO oxidation reaction which appears to be favoured as the reacting medium becomes more oxidising as opposed to the trend observed when operating under oscillating conditions. Nevertheless, changing the experimental conditions has no effect upon the HC oxidation reaction. This highlights the fact that there is probably a contribution from the NO + HC reaction. This phenomenon is the same as the one observed under oscillating conditions.

## 2. Activity of the Monometallic Catalysts

To ascertain the unusual behaviour of the bimetallic catalyst, a study of both monometallic catalysts was carried out under similar experimental conditions. Rhodium has been reported previously as an efficient catalyst for  $N_2O$  production (8); prior to further studies, this point was verified. In Fig. 3 the formation of  $N_2O$  for  $S_N = 1$  and under steady-state conditions is recorded. No  $N_2O$  production is observed upon Pt/ $Al_2O_3$  while it is formed

upon both Pt-Rh and Rh on alumina. Nevertheless, on the Pt-Rh/ $Al_2O_3$  catalyst, the conversion of NO into  $N_2O$  never exceeds 10% and decreases to zero for temperatures above 300°C. As anticipated, the formation of  $N_2O$  is more efficient upon the rhodium, but still does not exceed ca. 30%. Although in this case it is formed up to a higher temperature than on the Pt-Rh/ $Al_2O_3$  catalyst, the main process above 300°C is  $NO \rightarrow N_2$ . A further point to note is that the amount of  $N_2O$  formed on 1% Rh/ $Al_2O_3$  should be five times larger than on the Pt-Rh/ $Al_2O_3$  where the Rh content is only 0.2%. The experimental trace, published elsewhere (22), showed two waves of conversion; the first, at low temperature, corresponds mainly to  $N_2O$  formation, while the second, above 300°C, is characteristic of  $N_2$  formation only.

*Influence of the catalyst mass.* The influence of the mass on monometallic catalysts was studied employing the same conditions as in the case of the bimetallic, i.e., oscillating around the stoichiometry with a frequency of 0.05 Hz and an amplitude of 0.1. These results are shown in Figs. 4a and 4b and unlike the Pt-Rh, it can be seen that there is a direct correlation between mass and conversion for both platinum and rhodium for the three reactants. As mentioned in the previous section, if  $T_{50}$  is higher than 350°C, then NO is converted entirely into  $N_2$ .

*Influence of the reacting mixture.* The values of  $T_{50}$  under stationary conditions for different reacting compositions ( $S_N = 0.45, 1, \text{ and } 1.45$ ) are given in Table 5 for Pt/ $Al_2O_3$  and Rh/ $Al_2O_3$ , respectively. These data were compared with those for  $S_N = 1$  when cycling at 0.05 Hz. The catalytic behaviour of each metal was singularly different.

The platinum was not very efficient for the reaction of NO in reducing media when compared to rhodium, where the role of rhodium in catalytic converters becomes clear. In reducing media, all the reactions on rhodium were favoured when compared to the activity at stoichiometry or to the results obtained at  $S_N = 0.45$ . The consequence of the fact that the  $N_2O$  formation is favoured on rhodium

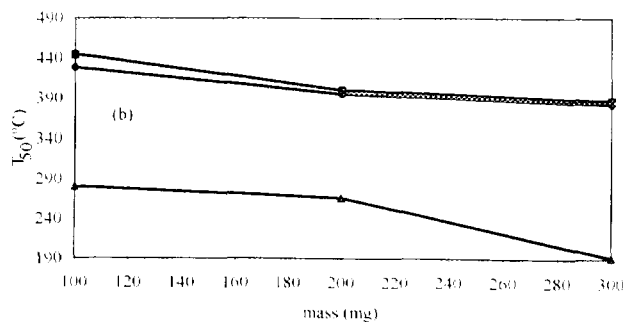
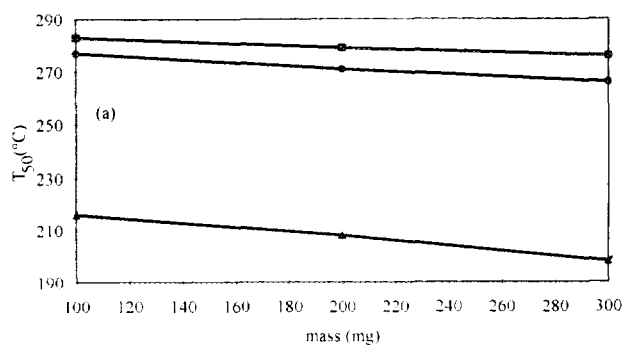


FIG. 4. Temperature of half-conversion of the three reactants as a function of catalytic mass ( $\blacktriangle$ ) CO, ( $\blacksquare$ ) NO, and ( $\bullet$ ) HC, for (a) Pt/ $Al_2O_3$  and (b) Rh/ $Al_2O_3$  under oscillating conditions at  $S_N = 1 \pm 0.1$  with a frequency of 0.05 Hz.

TABLE 5

Conversion Data Expressed as  $T_{50}$  ( $^{\circ}\text{C}$ ) for 100 mg Mono-metallic Pt/ $\text{Al}_2\text{O}_3$  or Rh/ $\text{Al}_2\text{O}_3$  under Steady-State and Oscillating Regimes

	$S_N = 0.45$	$S_N = 1$	$S_N = 1.45$	$S_N = 1^a$
		a. Pt/ $\text{Al}_2\text{O}_3$		
CO	298	220	216	216
NO	318	290	—	283
HC	27% <sup>b</sup>	279	307	277
		b. Rh/ $\text{Al}_2\text{O}_3$		
CO	229	253	275	280
NO	232	420	—	445
HC	43% <sup>b</sup>	401	377	428

<sup>a</sup> Oscillating.

<sup>b</sup> Maximum conversion reached.

at low temperature is that the difference of activity between platinum and rhodium observed at  $S_N = 1$  is somewhat exaggerated since Table 5 shows temperatures corresponding to the complete reduction of NO to  $\text{N}_2$ .

Most important, however, was the fact that for platinum, the CO oxidation was favoured under very oxidising conditions, whereas this activity decreased for rhodium. This result shows that at  $S_N = 1.45$  and for this range of temperatures (ca. 200–270 $^{\circ}\text{C}$ ) rhodium was oxidised and lost its activity, whereas platinum was less affected.

### 3. Isothermal Activity for $S_N = 1$

The experiment in Fig. 5 represents the light-off trace of CO dwelling at different temperatures (210 and 222 $^{\circ}\text{C}$ ) upon the Pt-Rh/ $\text{Al}_2\text{O}_3$  catalyst at  $S_N = 1$ . These temperatures were chosen in order to have comparable conversions under both stationary and oscillating feed. Note that the abscissa records units of time and that the time scale was different for each experiment. The effects observed at low conversion should not be taken into account be-

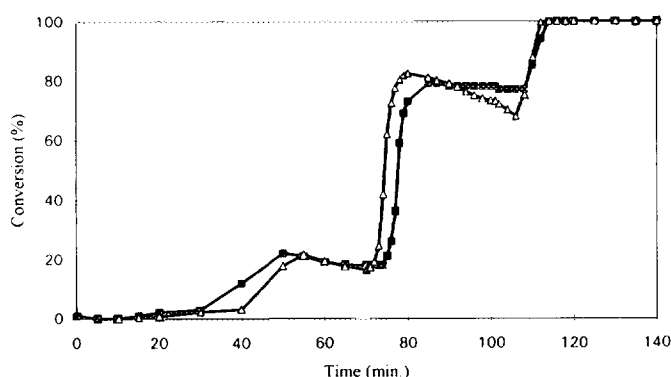


FIG. 5. Conversion of CO as a function of time on 100 mg of Pt-Rh/ $\text{Al}_2\text{O}_3$  at  $S_N = 1$  under (■) steady-state and (△) oscillating conditions with dwells of temperature at 210 and 222 $^{\circ}\text{C}$ .

cause an overshoot of the temperature (5 $^{\circ}\text{C}$ ), difficult to control in this range, was responsible for this apparent effect. Therefore, the shift in time as represented by the curve is not a phenomenon for consideration in this paper. At 222 $^{\circ}\text{C}$ , the temperature was monitored accurately at  $\pm 1^{\circ}\text{C}$ .

At high conversion, the activity remains unchanged with time when the catalyst operates under constant reactant feed, whereas under oscillating conditions, a deactivation with time is observed. As discussed above, the deactivation is a phenomenon associated with the oxidation of rhodium. Therefore, the loss of activity at a constant temperature must result from a progressive oxidation. This implies that the quantity of rhodium being oxidised during each complete cycle is greater than the quantity which is reduced and that the rate of oxidation is therefore greater than the rate of reduction.

### 4. Effect of the Nature of the Reactant on the Oxidation State: Step-Change Activity

The experiments described above suggest that the catalyst was affected by changes in the stoichiometry of the reacting media. Therefore it was decided to examine the response of the catalyst to step-changes in composition on the Pt-Rh/ $\text{Al}_2\text{O}_3$  catalyst. This is shown in Figs. 6a and 6b, respectively, for a catalyst treated at 300 $^{\circ}\text{C}$  under 1.1% CO/ $\text{N}_2$  or under 0.5%  $\text{O}_2$ / $\text{N}_2$ . The time constants as well as the peak areas are given in Table 6. The results described different behaviour according to the nature of the pretreatment:

(i) Oxidation step (CO- $\text{O}_2$ -CO). During the first transition (CO/ $\text{O}_2$ ), a rapid desorption of  $\text{CO}_2$  was observed within 1.3 min, which indicated that the  $\text{CO}_2$  was formed by a surface reaction. After 15 min under oxygen, the catalyst was subjected to the second transition ( $\text{O}_2$ /CO) and a second  $\text{CO}_2$  peak was observed. The desorption was completed in 6 min; this comparatively longer time suggests that the catalyst was already partially oxidised.

(ii) Reduction step ( $\text{O}_2$ -CO- $\text{O}_2$ ). Once again, two  $\text{CO}_2$

TABLE 6

Peak Areas and Peak Widths for the Oxidation Test and Reduction Test

Transition	Peak area (arb. units)	Peak width (min)
a. Oxidation Test		
CO/ $\text{O}_2$	$1.10 \times 10^4$	1.3
$\text{O}_2$ /CO	$3.31 \times 10^4$	6.0
b. Reduction Test		
CO/ $\text{O}_2$	$9.99 \times 10^4$	48.0
$\text{O}_2$ /CO	$1.79 \times 10^4$	1.5

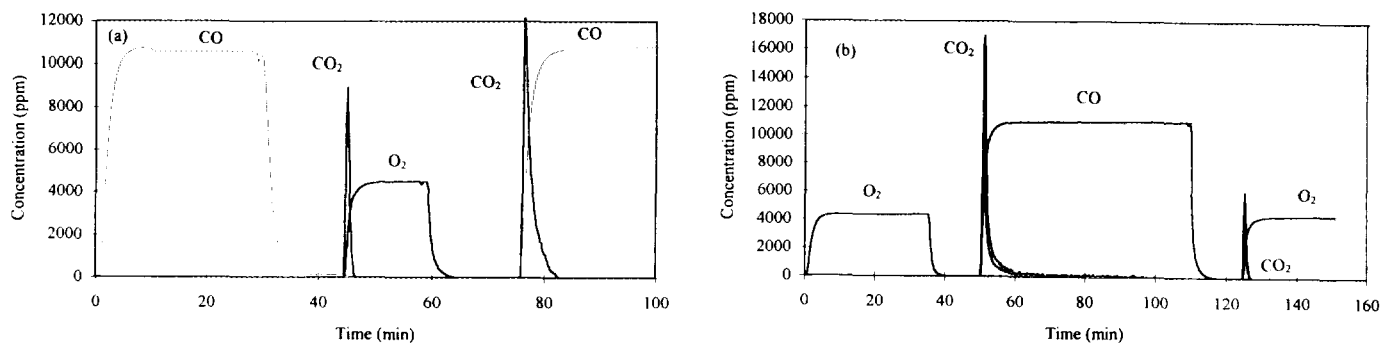


FIG. 6. Step-change activity recorded at 300°C: (a) oxidation reaction and (b) reduction reaction. Note that  $\text{CO}_2$  scale is multiplied by 10 (a) and by 5 (b).

peaks were observed but they were characteristically different from those observed for the oxidation step. Immediately after the first transition ( $\text{O}_2/\text{CO}$ ), a sharp peak was observed corresponding to the reaction between coadsorbed species. Nevertheless, the trace took ca. 48 min to return to the baseline. This suggested that during the oxygen pretreatment the bulk of the metallic phase was oxidised. After this period, the switching to CO encouraged the appearance of a sharp peak which had the same surface and baseline width as the one observed during the same transition in the oxidation step, i.e., 1.5 min.

#### 4. DISCUSSION

The Pt-Rh/ $\text{Al}_2\text{O}_3$  catalyst exhibits quite unusual behaviour when submitted to an oscillating feed of reactant since there is no straightforward explanation for the lack of correlation between mass and conversion. From this experimental observation, the following questions arise. Does the catalytic surface remain homogeneous during the reaction or are there changes? What is responsible for these changes and how fast do they occur? How does the reacting medium influence these modifications and are they a specific feature of the oscillating mode of action?

The answers to these questions lie within the following:

(i) the strength of the reacting composition disfavours CO oxidation with the bimetallic catalyst under oscillating but not stationary conditions;

(ii) in the case of rhodium alone, the CO oxidation is inhibited under oxidising conditions both under the cycling and stationary regimes;

(iii) in all cases, the CO oxidation is favoured with platinum.

The deactivation cannot be explained in terms of dispersion since the  $\text{CO}/\text{O}_2$  reaction is known to be structure insensitive (23) and because the dispersion of both rhodium and platinum is only slightly affected by cycling atmosphere treatments during the first 2 h. Also these

effects are limited for temperatures lower than 600°C (13, 14). Hence, under our experimental conditions, dispersion is not a justifiable explanation for the loss of activity.

The deactivation of the oxidation reaction upon rhodium could be explained by the formation of an inactive rhodium oxide formed during the lean transition. The inhibition of oxidation reactions and particularly those of CO are well known on oxides (24). The formation of  $\text{Rh}_2\text{O}_3$  has been observed by other workers and confirmed by XPS. However, that was under more strongly oxidising conditions (10, 25). The inhibiting effect of the oxygen concentration upon CO oxidation has been noted previously by several other groups (7, 26), but in slightly differing contexts. Under oxidising conditions, it would normally be expected that oxidation reactions would be favoured: however, as reported above with Fe, Co, and Ni/Pt alloy catalysts (26) or Pt-Rh catalysts (7), the oxidising medium has the effect of segregating the added metal, forming, in the case of the Pt-Rh catalyst, the relatively inactive  $\text{Rh}_2\text{O}_3$ , leading to a decrease in the activity of the  $\text{CO}/\text{O}_2$ . Moreover, Oh *et al.* (26) using *in situ* electron diffraction analysis, reported that after the segregation of the second metal, both the alloy and pure platinum are present.

One of the striking features of oscillating conditions is the speed at which the redox process occurs; indeed, we observe an inhibiting effect with a frequency of 1 Hz, implying that the effect is at least on the order of a second. Therefore, these experimental conditions could be used as a tool to measure the rate of any redox process taking place upon a surface. The fact that the catalyst is deactivated under stoichiometric conditions when at a constant temperature in the oscillating regime indicates clearly that the rate of the oxidation of the rhodium is greater than that of reduction. Also we can distinguish the difference in the effects of media by analysing the results of step-changes. The exposure of the prerduced catalyst to oxygen results in a fast response characterised by the production of  $\text{CO}_2$  formed by the surface reaction of preadsorbed

CO and oxygen. During the oxidative transition the process gradually seeps into the bulk of the metal as is proved by the time during which  $\text{CO}_2$  is produced after the CO transition. The redox process of the metal is obviously governed by the temperature and should also be related to the proportion of metal oxidised compared to the concentration of oxygen from the gas phase. This synergy between temperature and oxygen concentration accounts for the noncorrelation between mass and conversion. At some point, this phenomenon may reach an equilibrium and one can imagine that at temperatures in excess of  $550^\circ\text{C}$  the quantity of rhodium reduced and then oxidised during the whole transition becomes the same, leading to some correlation; nevertheless, at this point the conversion of 100% is no longer a means of probing the state of the metal.

As the heats of adsorption of oxygen are significantly different on platinum and rhodium, preferential adsorption of the reactant may occur on one of the metals in the bimetallic providing that this metal can be easily accessed by the oxygen in the reactant feed. Since there is low loading of rhodium in the bimetallic and a high  $H/M_1$  ratio, it is likely that the rhodium within this range of temperatures is easily oxidised and, as implied in the literature, oxidation is easier on small particles (27). Even in the case where rhodium is not completely isolated, and there is the alloy formation, this explanation still remains valid because even under mild oxidising conditions, it has been shown that there was a rhodium surface enrichment (28, 29). Also it is clear that there exists no synergistic enhancement of the activity and that during the temporary deactivation of the rhodium during the oxidative period, the activity is maintained by the unchanged platinum. The role of platinum is also important because of its contribution to the redox process. The reduced platinum probably assists the activation of oxygen upon rhodium during the lean transition and then provides active sites available for the CO adsorption during the rich transition. We have shown recently that the mode of preparation is the key factor in forming a bimetallic catalyst in which both metals are in close contact, a condition which is essential for undergoing a fast redox process (30). The temporary loss of activity due to the oxidation of the rhodium during the lean transition is probably compensated for in the normal catalyst in the presence of ceria. Also, Schlatter and Mitchell (31) have found that the formation of a surface rhodium oxide is particularly active for the water gas shift reaction contributing, therefore, to enhance the conversion of CO.

The behaviour of the bimetallic catalyst, whether oscillating at  $S_N = 1.45$  (i.e., between 1.35 and 1.55) or in the stationary regime with the same oxidising conditions, proved very intriguing. We cannot account for the oxygen inhibition under oscillating conditions and are therefore

unable to explain metal oxidation in one case but not in the other. Here again we shall remember that a global stoichiometry of 1.45 represents relatively mild oxidative conditions and that other researchers found that higher oxidant to reductant ratios (ca. 3.33) were necessary to observe the same rhodium oxidation under stationary conditions (10). For lower oxygen concentrations, the CO oxidation was favoured, as we observed, when  $S_N$  was increased.

The results obtained under the cycling operation implicate a transient phenomenon related to oxygen. This evokes the work of Kim *et al.* (32) who showed that the inhibition of an oxidation reaction is related to temperature-dependent variations of the form which the oxygen takes upon the surface. The reaction rate is of course related to the coverage by oxygen under steady-state conditions, but for transient experiments, the readiness to form  $\text{CO}_2$ , for example, at constant oxygen coverage, varies with the initial coverage of oxygen. This is interpreted in terms of oxygen structural difference. This difference may be due to some degree of disorder caused on the surface by the constant migration of oxygen from the bulk to surface and vice versa.

## 5. CONCLUSION

The catalytic activity of the  $\text{Al}_2\text{O}_3$ -supported Pt–Rh bimetallic catalyst was studied under reaction conditions representative of those occurring in a catalytic exhaust converter under both oscillating and steady-state conditions. The results were systematically compared with those obtained on the monometallics Pt and Rh supported on alumina.

At Pt–Rh catalyst exhibits intriguing behaviour when subjected to oscillations of the feed of the reacting mixture. Indeed, a strong deactivation was observed for the oxidation reaction of CO and  $\text{C}_3\text{H}_8$ . This deactivation is a function of the composition of the reacting medium and was monitored even under mild oxidative conditions and fast oscillations. The loss of activity is associated with an oxidation of the rhodium to its inactive form,  $\text{Rh}_2\text{O}_3$ . It was shown that a fast redox process of the rhodium occurs when switching from a reducing to an oxidising medium. During the lean phase, the activity is maintained by the platinum which remains unaffected. The gain in activity due to the contribution of the rhodium is only observed during the rich transition. The ease with which the rhodium is oxidised in a very short period seems to indicate that it is easily accessible to the oxygen of the gas phase, and/or the oxidation reaction of the metal is assisted by the platinum. Nevertheless, no clear evidence regarding the catalyst composition could be drawn but further physical studies currently in progress should verify the location of both metals.



This paper endeavours to elucidate the role of oxygen in the activation/deactivation processes of precious metals in three-way catalysis and gives interesting perspectives on the study of metal oxidation/reduction rates upon catalytic surfaces. Moreover, and still not fully understood, is the clear evidence that the behaviour of a catalytic surface under steady-state conditions is completely different from that under oscillating conditions even though the overall reacting medium is the same, implying that the very last layer of atoms could be strongly affected by the migration of oxygen occurring in the bulk of the metal.

Nevertheless, in a real exhaust gas, the presence of H<sub>2</sub>O and SO<sub>2</sub> could modify strongly the behaviour of this catalyst and the deactivation due to the redox process may be compensated for by parallel reactions to convert the exhaust pollutant. The effect of these components are currently being studied in our laboratory.

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