

## KINETICS, CATALYSIS, AND REACTION ENGINEERING

## Percentage of Metal Exposed on Commercial Three-Way Catalysts

Laurence Salin,<sup>†,‡</sup> Claude Potvin,<sup>†</sup> Jean-François Tempere,<sup>†</sup> Michel Boudart,<sup>§</sup>  
Gérald Djega-Mariadassou,<sup>\*,†</sup> and Jean-Michel Bart<sup>‡</sup>

Laboratoire Réactivité de Surface, Université P&M Curie, casier 178, CNRS URA 1106, 4 Place Jussieu, 75252 Paris, Cedex 05, France, PSA Peugeot-Citroën, DOGN/CGMP/CED, 18 rue des Fauvelles, BP 16, 92252 La Garenne-Colombes, Cedex, France, and Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025

A new sensitive method has been developed to determine the percentage of metal exposed (% ME) in commercial three-way bimetallic catalysts, fresh and aged. The method is based on the measurement of specific rates of two structure insensitive reactions: the hydrogenation of benzene and propene. Values of % ME were obtained for each metal at the surface of Pt–Rh and Pd–Rh catalysts with very low % ME. The % ME and the corresponding catalytic activity of the samples in the postcombustion follow the same trend as a result of aging.

## 1. Introduction

Typical automotive catalysts consist of Pt, Pd, and Rh supported on Al<sub>2</sub>O<sub>3</sub> with CeO<sub>2</sub>. The catalyst is wash-coated on a cordierite monolith; it is called a three-way catalyst as it abates three kinds of exhaust pollutants: hydrocarbons (HC), CO, and NO<sub>x</sub>. The purpose of this work is to devise a new method to determine the percentage of each metal exposed (% ME) at the surface of commercial catalysts, both fresh and aged.

In such an effect, available catalytic monolith must be crushed into homogenized powder samples. As a result, the total metal loading of such samples can be as low as ca. 0.2 wt %.

Chemisorption of H<sub>2</sub>, NO, or CO as well as physical techniques such as transmission electron microscopy are used to measure the size of clusters of Pt, Rh, and Pd on various supports.<sup>1–4</sup> From the average cluster size, % ME can be obtained. However, these methods are not sensitive enough for commercial three-way catalysts because of their low metal loading.

To determine the percentage of metal exposed (% ME) under these demanding conditions, a new method based upon the kinetics of structure insensitive reactions was developed. It was first applied to titration of metallic rhodium supported over ceria alone.<sup>5,6</sup> In the present work this method is extended to commercial bimetallic Pt–Rh and Pd–Rh catalysts. A reaction is called structure insensitive when the turnover rate  $v_t$  defined as the rate per exposed metal atom per second, is independent of metal cluster size in the range from 1 to 10 nm.<sup>7</sup> The turnover rate does not depend on the method of catalysts preparation and is not influenced by the presence of inert additives or the nature of the

crystal face exposed.<sup>8,9</sup> Since all exposed metallic atoms are considered as active sites, their quantity  $L$  (micromoles per gram of catalyst) can be easily obtained from the specific rate  $v_{sp}$  (micromoles per second per gram of catalyst), if the turnover rate is known independently under the same conditions of reaction.

$$L = v_{sp}/v_t \quad (1)$$

Since the present work deals with bimetallic catalysts, two structure insensitive reactions were used; the hydrogenation of benzene and propene. This procedure is the principle behind the new method of characterization of bimetallic catalysts. For each reaction the turnover rate and activation energy were determined over reduced Pt, Rh, and Pd supported on silica and compared with literature values.<sup>5,10–14</sup> Furthermore, to take into account the possibility of alloy formation, the turnover rate for the benzene reaction was also determined for silica-supported bimetallic Pt–Rh alloy catalysts.

Fresh and aged Pt–Rh and Pd–Rh commercial catalysts supplied by Peugeot Société Anonyme (PSA) were used with both structure insensitive reactions. Aging was conducted in the laboratory as well as in the engine under real conditions of use.

## 2. Experimental Section

**2.1. Reference Catalysts.** Catalysts with metal concentrations between 0.3 and 5 wt % were prepared. Samples (Pt/SiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Pd/SiO<sub>2</sub>) noted as "reference catalysts" were prepared by incipient wetness impregnation of silica (Aerosil Degussa 380, 380 m<sup>2</sup>·g<sup>−1</sup>) with an aqueous solution of metal precursor (H<sub>2</sub>PtCl<sub>6</sub>, RhCl<sub>3</sub>·3H<sub>2</sub>O, and PdCl<sub>2</sub> supplied by Merck 99.995 pure). Silica-supported Pt–Rh reference catalysts were also prepared by coimpregnation in order to estimate the

\* E-mail: djega@ccr.jussieu.fr. Fax: (33) 01 44 27 60 33. Tel: (33) 01 44 27 36 26.

<sup>†</sup> Université P&M Curie.

<sup>‡</sup> PSA Peugeot-Citroën.

<sup>§</sup> Stanford University.

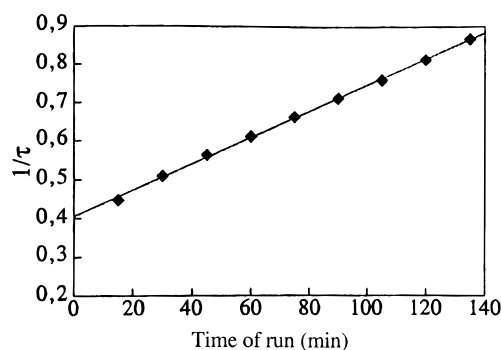
turnover rate of the Pt–Rh alloy in the molecular probe reactions. In all cases the metal precursor solution was added:  $2 \text{ cm}^3 \cdot \text{g}^{-1}$  of silica and the sample was dried in air at 343 K for 4 h after impregnation.

Commercial catalysts were obtained from PSA. They contained noble metals dispersed on a washcoat containing alumina, ceria (4–10 wt %) and promoters deposited on monolithic supports. Two kinds of catalysts were studied: Pt–Rh and Pd–Rh supported catalysts with weight ratios of 5/1 and 7/1, respectively, and a total metal loading of 0.2 wt %. Pd–Rh catalysts were multilayered catalysts: the two metals are introduced in two separate phases, to avoid the formation of alloys. The commercial catalysts were crushed and sieved (particle size  $<80 \mu\text{m}$ ) to get a powder representative of the whole washcoat supported on the monolith.

Fresh catalysts, as supplied, were aged to follow the stability of accessible metallic sites and the evolution of the catalytic activity in CO and HC oxidation and NO reduction. Laboratory aging procedures were undertaken to investigate the damage resulting from high-temperature treatments. Aging referred to as A1 is an 8 h thermal treatment in a 10 vol %  $\text{H}_2\text{O}$ – $\text{N}_2$  mixture at 1173 K. For A2 aging, the catalysts were aged for 32 h under the same mixture at 1373 K. Real gas exhaust aging in an engine referred to as B aging, was also carried out over 138 h. Before each run fresh and aged catalysts were pretreated at 673 and 373 K, respectively, in flowing  $\text{H}_2$  ( $6 \text{ L} \cdot \text{h}^{-1}$ ) for 30 min.

**2.2. Measurement of Reaction Rates.** The rates of gas-phase hydrogenation of benzene and propene were measured at atmospheric total pressure. Flow rates were controlled by mass flow meters. Hydrogen (Air Liquide, purity: 99.995%) was purified by passing through an oxygen trap (Oxysorb, Air Gaz). Benzene supplied by Merck (spectroscopic quality) contained no detectable thiophene by mass spectrometry. The feed rate ( $6 \text{ L} \cdot \text{h}^{-1}$ ) was sent to a Pyrex reactor loaded with 0.4–0.8 g of catalyst on sintered glass 1 cm in diameter. The temperature of the reaction was measured with a Chromel–Alumel thermocouple placed at the center of the catalyst bed 0.4 cm thick with  $80 \mu\text{m}$  grains. For benzene hydrogenation, the specific rate was measured from 293 to 373 K under differential conditions. For propene hydrogenation, a temperature of 195 K was chosen to work under differential conditions. The composition of the effluent was analyzed with a HP 5890 series II gas chromatograph equipped with a capillary column and a flame ionization detector. The column was kept at 313 K with a helium carrier at a flow rate of  $0.6 \text{ L} \cdot \text{h}^{-1}$ . The partial pressure of benzene and propene was 50 Torr (760 Torr = 101.3 kPa). The only observed products were cyclohexane and propane, respectively. Before each run the catalyst was pretreated at 373 K in flowing  $\text{H}_2$  ( $6 \text{ L} \cdot \text{h}^{-1}$ ) for 30 min.

As the catalysts suffered deactivation during reactions, the initial conversion was determined according to a second-order deactivation law: the reciprocal value of the conversion  $\tau$  versus time  $t$  of the run (eq 2) was used to determine (Figure 1) the initial conversion  $t_0$



**Figure 1.** Reciprocal value of the conversion  $\tau$  versus time  $t$  of run.

by extrapolation to zero time

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \kappa\tau \quad (2)$$

where  $\kappa$  is an empirical deactivation constant.<sup>15–17</sup>

The activity of commercial fresh and aged catalysts in postcombustion reaction was checked at PSA. The feed was a synthetic gas mixture representative of real gasoline exhaust gas. Measurements with preheated feed between 343 and 723 K in lean and rich mixtures were carried out on catalysts to determine the temperature of light-off, defined as the temperature at 50% conversion of the pollutant. The three pollutants CO, HC, and  $\text{NO}_x$  were controlled.

**2.3. Hydrogen Chemisorption.** Experiments were carried out at 313 K in a conventional high-vacuum system equipped with a Datametrix (1014 A type) capacitance gauge. Prior to measurements, the catalysts were reduced under flowing  $\text{H}_2$  for 2 h at 773 K for platinum- and rhodium-based catalysts and at 573 K for the Pd catalyst. Then, they were evacuated at reduction temperature for 1 h. The “back-sorption” method was used<sup>18</sup> and the value of % ME was calculated on the basis of a H/Metal ratio equal to unity. For the palladium-based catalyst, only the first linear portion of the isotherms (below 25 Torr) was retained to stay away from the formation of the  $\beta$ -Pd hydride phase<sup>19–21</sup> at higher partial pressure of hydrogen at 313 K.

### 3. Results and Discussion

#### 3.1. Turnover Rates and Activation Energy of the Two Probe Reactions on Reference Catalysts.

The turnover rates of benzene and propene hydrogenation over the three metals were determined on reference catalysts (Table 1). Silica-supported rhodium reduced over 2 h in flowing hydrogen at 773 K hydrogenates benzene at 323 K, the turnover frequency equaling  $0.21 \text{ s}^{-1}$ , corresponding to  $0.04 \text{ s}^{-1}$  at 293 K, whereas as shown by Sivak and Muetterties,<sup>22</sup> rhodium engaged in allyl complexes can also achieve complete benzene hydrogenation but displays turnover rates 30 times lower at 293 K. So, it can be deduced that the hydrogenating character of reduced rhodium is linked to its metallic state. Concerning platinum or palladium, at the oxidized state, we have no values of turnover rates and we assumed, as for rhodium, that only metallic Pt and metallic Rh are active in hydrogenation. The monometallic reference catalysts allowed us to determine  $v_i$  for each metal, the  $v_i$  value of the

**Table 1. Turnover Rates of Benzene and Propene Hydrogenations over Reduced Pt, Rh, Pd, and Pt–Rh Silica-Supported Catalysts**

samples	H <sub>2</sub> chemisorption (313 K)		benzene hydrogenation (323 K)			propene hydrogenation (195 K)	
	wt %	L, $\mu\text{mol}$ of sites $\cdot \text{g}_{\text{cat}}^{-1}$	$v_{\text{sp}}$ , $\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$	$v_t$ , $\text{s}^{-1}$	$E$ , $\text{kJ} \cdot \text{mol}^{-1}$	$v_{\text{sp}}$ , $\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$	$v_t$ , $\text{s}^{-1}$
Pt	1.49	31	6.6	0.21	47.4	1	0.03
Rh	1.73	100	21	0.21	43.6	<i>a</i>	<i>a</i>
Rh	0.35	35				31	0.88
Pd	3.19	35	0.035	0.001	53.2	<i>a</i>	<i>a</i>
Pd	0.26	8.5	<i>a</i>	<i>a</i>		3.4	0.40
Pt–Rh	3.88 for Pt 0.71 for Rh	2.7	0.49	0.18	46.8		

<sup>a</sup> Too low or too high metal loading.

**Table 2. Turnover Rate ( $v_t$ ) and Apparent Activation Energy ( $E$ ) of Benzene and Propene Hydrogenation over Reduced Pt, Rh, Pd, and Pt–Rh Silica-Supported Catalysts: Literature Values**

catalysts	benzene		propene $v_t$ , $\text{s}^{-1}$	ref
	$v_t$ , $\text{s}^{-1}$	$E$ , $\text{kJ} \cdot \text{mol}^{-1}$		
Pt/Al <sub>2</sub> O <sub>3</sub>	0.22	40	0.02	Basset et al. <sup>11</sup>
	0.11–0.27	43–54		Flores et al. <sup>13</sup>
		38		Antonucci et al. <sup>26</sup>
Rh/Al <sub>2</sub> O <sub>3</sub>	0.21	37	0.3	Rorris et al., <sup>25</sup> Burwell et al. <sup>24</sup>
Rh/SiO <sub>2</sub>	0.22	35.6		Fuentes et al., <sup>12</sup> Fajardie et al. <sup>5</sup>
Pd/CeO <sub>2</sub>		48.9		Marques Da Cruz et al. <sup>10</sup>
Pd/SiO <sub>2</sub>	0.001	50		Kepinski et al. <sup>27</sup>
	0.001			Del Angel et al. <sup>14</sup>
				Chou et al. <sup>23</sup>
				Rorris et al., <sup>25</sup> Burwell et al. <sup>24</sup>

Pt–Rh alloy was determined on bimetallic Pt–Rh reference catalysts. As Pd–Rh commercial catalysts were multilayered catalysts, Pd and Rh were deposited on different support layers and the Pd–Rh alloying was not considered. Typically, the determination of the turnover rate proceeded as follows:  $L$ , for a given reference catalyst, was determined by hydrogen chemisorption, and  $v_{\text{sp}}$  was obtained on the same weight of catalyst in benzene and propene hydrogenation at standard conditions (section 2.2). Equation 1 gives directly the value of the turnover rate.

The value of the turnover rate of Pt and Rh for benzene hydrogenation is in agreement with the literature data (Tables 1 and 2). For palladium, data in Table 1 show that its turnover rate ( $0.001 \text{ s}^{-1}$ ) is about 200 times lower than those of Pt and Rh ( $0.21 \text{ s}^{-1}$ )<sup>14,23</sup> at 323 K. Because of its very low value of  $v_t$ , the contribution of Pd was neglected in benzene hydrogenation over a catalyst containing also Pt or Rh.

For propene hydrogenation, the following  $v_t$  values were obtained: Pd ( $0.40 \text{ s}^{-1}$ ), Rh ( $0.88 \text{ s}^{-1}$ ), and Pt ( $0.03 \text{ s}^{-1}$ ) (Table 1). The turnover rate over palladium and platinum supported on alumina and silica have been determined<sup>24–27</sup> in experimental conditions very close to ours ( $T = 220 \text{ K}$  for Pt;  $T = 201 \text{ K}$  for Pd;  $\text{H}_2/\text{C}_3\text{H}_8 = 12$ ). Extrapolation of their data at 195 K, using their calculated apparent activation energy ( $36.3 \text{ kJ} \cdot \text{mol}^{-1}$  for Pt and  $32.3 \text{ kJ} \cdot \text{mol}^{-1}$  for Pd) led to turnover rates of  $0.3 \text{ s}^{-1}$  for Pd and  $0.02 \text{ s}^{-1}$  for Pt (Table 2), in good agreement with our results.

The main interest for characterizing samples by two structure insensitive reactions is to make possible the separate counting of each metal active site in a bimetallic catalyst. For the commercial Pd–Rh catalyst, accessible Pd and Rh atoms are counted without distinction in propene hydrogenation. The turnover rate of Rh and Pd in propene hydrogenation being 0.88 and  $0.40 \text{ s}^{-1}$ , respectively (Table 1), the specific rate of Rh–Pd catalyst in propene hydrogenation,  $v_{\text{sp}}(\text{p})$ , is the sum of the  $v_{\text{sp}}(\text{p})$  of both metals, as shown in eq 3.

$$v_{\text{sp}}(\text{p}) = 0.88L_{\text{Rh}} + 0.40L_{\text{Pd}} \quad (3)$$

The values of  $v_t$  for Rh and Pd in benzene hydrogenation being 0.22 and  $0.001 \text{ s}^{-1}$ , respectively, Pd contribution to the specific rate of Rh–Pd catalyst in this reaction can be neglected. Therefore, the specific rate for benzene hydrogenation,  $v_{\text{sp}}(\text{b})$ , is given by eq 4:

$$v_{\text{sp}}(\text{b}) = 0.21L_{\text{Rh}} \quad (4)$$

leading directly to  $L_{\text{Rh}}$  determination. From eqs 3 and 4, it is therefore easy to calculate  $L_{\text{Pd}}$ , as shown by eq 5:

$$L_{\text{Pd}} = \frac{(v_{\text{sp}}(\text{p}) - 0.88[v_{\text{sp}}(\text{b})/0.21])}{0.4} \quad (5)$$

The same kind of calculations can be applied for Pt–Rh catalysts to determine  $L_{\text{Pt}}$  and  $L_{\text{Rh}}$ .

Furthermore, the absence of any alloy effect on turnover rates that could disturb the counting was confirmed by measuring the turnover rate of bimetallic Pt–Rh catalysts in benzene hydrogenation. The presence of alloy was shown by X-ray diffraction patterns and TEM-EDX analysis. It can be seen (Table 1, Pt–Rh/SiO<sub>2</sub> catalyst) that the value of  $v_t$  obtained for bimetallic catalysts ( $0.18 \text{ s}^{-1}$ ) is very close to that for monometallic ones ( $0.21 \text{ s}^{-1}$ ). This result justifies the use of eq 1 for determining % ME on bimetallic materials with a relative accuracy of 5%.

Moreover, benzene hydrogenation was carried out from 293 to 393 K and the apparent activation energy  $E$  was determined for Pt, Rh, and Pd in this temperature range on reference catalysts. The Arrhenius plot remains linear in the temperature range, and the values of  $E$  (Pt,  $47.4 \text{ kJ} \cdot \text{mol}^{-1}$ ; Pd,  $53.2 \text{ kJ} \cdot \text{mol}^{-1}$ ; Rh,  $43.6 \text{ kJ} \cdot \text{mol}^{-1}$ ) are in good agreement with those of other authors (Pt,  $38$ – $54 \text{ kJ} \cdot \text{mol}^{-1}$ ; Pd,  $48$ – $50 \text{ kJ} \cdot \text{mol}^{-1}$ ; Rh,  $36$ – $37 \text{ kJ} \cdot \text{mol}^{-1}$ ) (Tables 1 and 2). The value of  $E$  for bimetallic Pt–Rh reference catalysts ( $46.8 \text{ kJ} \cdot \text{mol}^{-1}$ ) can be considered as equal to that of monometallic catalysts



**Table 3. Percentage of Metal Exposed (% ME) on Commercial Catalysts versus Agings**

aging treatment	Pt–Rh		Pd–Rh	
	Pt	Rh	Pd	Rh
fresh	54	29	15	96
A1: 1173 K, 8 h	2.6	7.7	5.3	1.0
A2: 1373 K, 32 h	2.3	7.4	1.0	0.5
B: engine aging	2.5	9.2	0.9	1.1

within experimental error. Thus, the turnover rate in benzene hydrogenation, for Pt–Rh catalysts, could be extrapolated at any temperature from  $v_i$  for Pt and Rh at 323 K ( $0.21 \text{ s}^{-1}$ ) and the average value of  $E$  calculated from  $E$  for Pt, Rh, and Pt–Rh catalysts.

**3.2. Determination of the % ME on Commercial Catalysts.** Hydrogenation of benzene and propene was carried out over fresh and aged Pt–Rh and Pd–Rh catalysts to determine the % ME of these materials, as described in the preceding section. Table 3 reports the main results. Aging drastically lowered the % ME in each case. Furthermore, for a given bimetallic catalyst, the first metal shows a % ME different from the second one present in the material. This fact is particularly underscored for fresh Pd–Rh catalysts.

For Pt–Rh catalysts, the three modes of aging A1, A2, and B led to about the same % ME for a given metal after each treatment. This is not the case for Pd–Rh catalysts: the % ME is about 5% for Pd after A1 treatment, but only 1% after A2 and B ones, while the % ME for Rh remained 0.5% after A2 and about 1% after A1 and B agings. Finally, the common component of both catalysts, Rh, did not present the same % ME for equivalent aging: 8% for Pt–Rh and 1% for Pd–Rh. All these observations illustrate the incisiveness of the method for determining % ME.

**3.3. Commercial Catalyst Activity in the Reduction of NO and Oxidation of CO and HC.** Aged samples were submitted to catalytic runs in a test bench from 343 K up to 723 K (light-off conditions) in a CO, NO, O<sub>2</sub>, HC (C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>), CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> mixture, representative of real exhaust gases from a gasoline engine. The light-off temperature ( $T_{lo}$ ) of NO (0.095%) was determined with rich mixtures ( $R = 1.02$ ), whereas  $T_{lo}$  of CO (0.4%) and HC (0.05%) were evaluated with lean mixtures ( $R = 0.98$ ).

Values of  $T_{lo}$  of aging catalysts vary between 566 K and more than 723 K. The more difficult reaction to achieve is the NO reduction: for A<sub>2</sub> aging at 723 K, 50% of conversion is not reached for both catalysts, as is the case for B aging with the Pd–Rh catalyst. The oxidation reactions are easier, CO being oxidized at a lower temperature than HC. "Easy" and "difficult" refer to low and high  $T_{lo}$ , respectively.

Considering that the higher is  $T_{lo}$ , the lower is the corresponding activity, let us first classify Pt–Rh and Pd–Rh catalysts after aging, according to increasing  $T_{lo}$  of CO, NO, and HC:

catalyst after A1 > catalyst after B >  
catalyst after A2

It can be more particularly emphasized that the A2 treatment (32 h in flowing 10 vol % H<sub>2</sub>O–N<sub>2</sub> mixture at 1373 K) led to higher  $T_{lo}$  values and so appears to be a quite more severe treatment than B aging (138 h on an engine bench), leading to lower  $T_{lo}$ 's. Furthermore, it can be pointed out that Pd–Rh catalysts present

slightly lower  $T_{lo}$ 's of HC than Pt–Rh catalysts whereas the reverse situation is observed for  $T_{lo}$ 's of CO and NO.

**3.4. Comparison between % ME and the Activity of Commercial Catalysts in the Conversion of an Exhaust Gas Mixture.** One of the objectives of this work was to study if the % ME could be correlated to the activity of catalysts either for CO, NO, or HC reactions. The decomposition of NO and the oxidation of CO are well-known to occur on rhodium.<sup>28</sup> In our case, NO conversion over Pt–Rh catalysts with about 8% Rh exposed after A1, A2, and B agings (Table 3) are possible as well as Pd–Rh catalysts with only about 1% Rh exposed for the same agings. The difference of % Rh exposed between the two catalysts, for equivalent agings, can be explained by a difference in the washcoat technology. For Pd–Rh catalysts, comparison of % ME shows that both parameters follow the same trend: the A<sub>1</sub> catalyst with the higher % ME presents the greater activity as compared to A<sub>2</sub> or B aging.

## 4. Conclusion

A method for counting metallic atoms exposed in commercial three-way catalysts was developed in this study. Two structure insensitive reactions were used and the corresponding specific rates led directly to % ME. Moreover, this method made it possible, for bimetallic catalysts, to evaluate the respective % ME of each metal. The percentage of accessible metal for aged catalysts was very low, but the technique permitted us to titrate both metals exposed. After aging, the same trends are observed for % ME and activity of NO, CO, and HC conversion.

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