

Benzene Hydrogenation as a Tool for the Determination of the Percentage of Metal Exposed on Low Loaded Ceria Supported Rhodium Catalysts

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Benzene hydrogenation, a structure insensitive reaction, was used to determine the percentage of metal exposed on low loaded ceria supported rhodium 0.15 to 0.33 wt% Rh/CeO₂ catalysts. Catalysts were prepared from nitrated and chlorinated precursors. Freshly prepared catalysts and catalysts aged in air at 1173 K were studied. Hydrogen chemisorption carried out at 313 K on the chlorinated catalysts could be used to confirm the technique since, due to the presence of Cl⁻ ions on the samples, no hydrogen spillover was observed after reduction at 773 K. Data obtained from benzene hydrogenation were found to be in very good agreement with the percentages of metal exposed as calculated from hydrogen chemisorption measurements. Benzene hydrogenation was able to count very low percentages of metal exposed and it was shown from the data obtained for the nonchlorinated catalysts that, unlike hydrogen chemisorption, it was not disturbed by the hydrogen spillover occurring on some Rh/CeO₂ systems. The stability of the metal phase was investigated when rhodium was deposited on both high and low surface area ceria. It appeared that anionic exchange on a low specific surface area ceria could lead to a catalyst which, after calcination at 1173 K and reduction at 773 K, exhibits the same amount of exposed metallic rhodium atoms compared to a catalyst prepared from a high specific surface area ceria, hence, containing 50% more rhodium. © 1996 Academic Press, Inc.

INTRODUCTION

Engine exhaust emissions contribute widely to air pollution, and therefore many research programs are currently undertaken to produce catalysts capable of eliminating noxious gases from these exhaust streams. Today three-way catalysts are commonly used. A three-way catalyst is regularly composed of a temperature-resistant monolithic support coated with a mixture of alumina and rare earth oxides on which one or more noble metals are deposited (1). However, the increasing complexity of the systems used today (i.e., several noble metals supported on modified oxide

supports) results in great difficulty in the understanding and optimisation of these catalysts. To understand these systems it is first necessary to have a good knowledge of simple ceria supported monometallic systems before approaching more complex compositions. The understanding of the metal-support interactions of such systems should lead to the key factors involved in the catalytic process.

The present Rh/CeO₂ system was studied for the important roles played by both ceria and rhodium in the three-way catalysts. Namely, ceria content is observed to increase in the washcoat compositions because of its ability to promote the water-gas shift reaction and to store oxygen under lean conditions for use under rich conditions (2). Rhodium was selected for its promoting effect in the reduction of NO_x to N₂ (1, 3).

Catalyst preparation and metal loadings were chosen to obtain systems as close as possible to the composition and preparation of *commercial* catalysts. Catalysts were prepared by anionic exchange of chlorinated rhodium complexes, and low metal loadings were used (0.15 to 0.35 wt% of the oxide support).

It is well known that the characterization of rhodium catalysts by conventional techniques, such as hydrogen or CO chemisorptions and transmission electron microscopy, is difficult. In the case of hydrogen chemisorption, the hydrogen spillover generally observed on Rh/CeO₂ systems prevents any evaluation of the metal dispersion at room temperature (4–7). Bernal *et al.* (4, 8) have, however, shown that the spillover effect could be blocked by working at lower temperatures (i.e., 191 K). They also differentiated catalysts prepared by impregnation from nitrated precursors (i.e., Rh(NO₃)₃) and catalysts prepared from chlorinated precursors (i.e., RhCl₃ · 3H₂O). In the first case they showed that the kinetics of the spillover process were very sensitive to the specific pretreatment conditions (4) and that the spillover rate was found to decrease with increasing reduction temperature (7). The spillover contribution was rather small in the case of low surface area ceria supports (about 10 m² · g⁻¹) (9). Concerning Rh/CeO₂ catalysts

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prepared by impregnation from a $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ solution, they showed that the use of rhodium chloride as precursor could block the spillover process and make significant the hydrogen chemisorption at room temperature, independent of the reduction temperature (10).

In the case of CO chemisorption, the support itself can significantly adsorb CO and the stoichiometry for CO/Rh adsorption can vary (possibility of linear and geminal configurations on Rh(0)) (5, 11–15) so that it is difficult to evaluate the amount of CO adsorbed onto the metal phase. Therefore conventional chemisorption techniques cannot be used in a straightforward way to characterize ceria supported rhodium catalysts.

Several high resolution transmission electron microscopy (HRTEM) studies have been carried out to directly study the microstructure and size of the supported rhodium particles. Despite the difficulties in observing rhodium particles on ceria (low contrast), HRTEM was found to be a powerful tool in evidencing “decoration” effects and epitaxial relationships between Rh(0) particles and ceria (16, 17). Average particle sizes have been recently estimated by HRTEM (5, 9). Nevertheless most of these studies concerned systems containing relatively high rhodium contents (1 to 5 wt% of rhodium) generally supported on low surface area ceria supports. These metal loadings facilitate the observation of rhodium particles but are not in line with the commercial low metal loadings of three-way catalysts. The low loadings of the present catalysts (0.15 to 0.35 wt%) made the HRTEM study more difficult (18), already limited by the poor contrast existing between metallic rhodium and the ceria support. The limited number of metal particles, observed on the catalysts reduced at 773 K, prevented us from evaluating any precise average particle size. However, for a given sample, the observed aggregates generally exhibited similar sizes. Hence, considering that, if larger particles existed they would have been detected, the diameters measured were taken as upper values for the Rh(0) particle sizes.

For these reasons we searched for a technique able to determine the percentage of rhodium atoms exposed without being restricted by the possible spillover process, the low metal loadings, and the high specific surface areas of the oxide supports.

In this paper benzene hydrogenation is presented as a tool for counting the accessible metallic rhodium atoms (Rh(0)) of the low loaded ceria supported rhodium catalysts. This reaction was chosen for its structure insensitivity (19–21). As shown by Boudart *et al.* (22), for a structure insensitive reaction the turnover rate (number of reagent molecules converted per second and per catalytic site) does not depend on the particle size or crystallographic plane. In these conditions, all the exposed metallic atoms are considered as active sites. Consequently the turnover rate (V_T) is directly related to the number of catalytic sites

by the following relation:

$$\text{Turnover rate (s}^{-1}\text{)} = \frac{\text{reaction rate (mole C}_6\text{H}_{12} \cdot \text{s}^{-1} \cdot \text{g}^{-1}\text{)}}{\text{number of active sites (mole} \cdot \text{g}^{-1}\text{)}} \quad [1]$$

The number of metallic active sites can be easily calculated from the reaction rate if the turnover rate is known at the temperature of the reaction. The total number of rhodium atoms present in the catalyst leads to the percentage of metal exposed.

This technique was applied to unaged low loaded rhodium CeO_2 supports (high and low specific surface area supports), as well as to a low loaded rhodium catalyst calcined at high temperature (1173 K).

EXPERIMENTAL

The ceria used was a standard high specific surface area cerium oxide ($144 \text{ m}^2 \cdot \text{g}^{-1}$) supplied by Rhône-Poulenc. It was used for EUROII three-way catalysts (models of years 1993 to 1995). A low specific surface area ceria ($6 \text{ m}^2 \cdot \text{g}^{-1}$) was prepared by calcining the high surface area ceria in air. The calcination process was as follows: ceria was heated to 673 K at a rate of $420 \text{ K} \cdot \text{h}^{-1}$ and was held at this temperature for 6 h. The temperature was then increased to 1173 K with the same heating rate and the sample was held to this temperature for 6 h. Finally the sample was cooled to room temperature in flowing air.

The Rh(Cl)/ CeO_2 catalysts were prepared by anionic exchange from an acidic solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson-Matthey) adjusted with HCl at pH = 1.9. The amount of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ introduced into the solution was calculated to obtain metal loadings of 0.35 wt%. After the ionic exchange the samples were filtered, washed with distilled water, and dried in air for 3 h.

Three ceria-supported rhodium catalysts were prepared by anionic exchange and are here after referred to as: Rh(Cl)/ CeO_2 E, Rh(Cl)/ CeO_2 CE, Rh(Cl)/ CeO_2 EC.

The Rh(Cl)/ CeO_2 E sample was obtained from the high surface area ceria ($144 \text{ m}^2 \cdot \text{g}^{-1}$). This sample contained 0.33 wt% Rh.

The Rh(Cl)/ CeO_2 CE sample was prepared from the low surface area ceria ($6 \text{ m}^2 \cdot \text{g}^{-1}$) to study the behaviour of the metal phase deposited over a stabilized CeO_2 support. It contained 0.15 wt% Rh.

In the case of a reduced sample the capital letter “R” is added to the nomenclature (Ex. Rh(Cl)/ CeO_2 CER refers to a calcined ceria exchanged from RhCl_3 and further reduced in H_2).

For both preparations the anionic exchange with rhodium complexes was reproducible (Table 1).

The Rh(Cl)/ CeO_2 EC sample was obtained by calcination of the Rh(Cl)/ CeO_2 E sample (calcination treatment similar to that described above).

TABLE 1
Characteristics of Samples

	CeO ₂	CeO ₂ C	Rh(Cl)/CeO ₂ E/ER	Rh(Cl)/CeO ₂ EC/ECR	Rh(Cl)/CeO ₂ CE/CER	Rh(N)/CeO ₂ I/IR	Rh/SiO ₂ I/IR
BET surface (m ² · g ⁻¹)	144	6	130 ^a /95 ^b	19/19	8/8	130/95	330/325
Rh (wt%)	—	—	0.31–0.33 ^c	0.33	0.15	0.40	0.33
Exchange yield (%) ^d	—	—	89–94	—	43	—	—

Note. E, exchanged; C, calcined in air (6 h at 673 K + 6 h at 1173 K); R, reduced in H₂ (5 liters/h) for 2 h at 773 K (180 K · h⁻¹); I, impregnated.

^a BET surface of the unreduced sample.

^b BET surface of the reduced sample.

^c Several samples were prepared and the percentage of rhodium exchanged varied from 0.31–0.33 wt%.

^d Yield of the anionic exchange relative to the 0.35 wt% Rh expected.

A Rh(N)/CeO₂ catalyst was prepared by an incipient wetness impregnation technique using an aqueous solution of Rh(NO₃)₃. The ceria used was the high surface area ceria (144 m² · g⁻¹). The precursor/support system was dried in air at 393 K for 3 h. To eliminate nitrates, it was further treated at 673 K in a flow of O₂ for 1 h, followed by 1 h in argon before cooling to room temperature. The surface area of the ceria sample did not significantly change during the treatments applied above. The metal loading obtained was 0.4 wt%. This catalyst was prepared to study the effect of hydrogen spillover on benzene hydrogenation and hydrogen chemisorption.

A Rh/SiO₂ reference sample was also prepared by wet impregnation of a high specific surface area silica (Aerosil Degussa 380, 380 m² · g⁻¹) with an aqueous solution of RhCl₃ · 3H₂O. Two cubic centimeters of rhodium solution were added per gram of silica. After impregnation the sample was dried in air at 343 K for 4 h.

Benzene hydrogenation measurements were carried out under a total pressure of 760 Torr in a conventional differential dynamic micro reactor. The flow rates were controlled by mass flowmeters. The total flow rate was set to 6 liter/h. The partial pressure of benzene was 51.8 Torr (760 Torr = 1 atm = 101.3 kPa). It was checked that within the temperature range used for the measurements of the percentages of metal exposed (323 K and 388 K) the order relative to benzene remained constant and equal to zero. Note also that in this domain the activation energy remained constant so that no change in the reaction mechanism was expected (Fig. 1). Benzene was analyzed with a Hewlett Packard Model 5890 Ser. II gas chromatograph equipped with a capillary column 50 m in length (0.2 mm i.d., 0.5 μm film thickness). A flame ionization detector was used. The column was provided by Hewlett Packard and contained cross-linked methyl-silicone. It was operated at 313 K with a flow rate of 0.06 liter/h of helium carrier gas. The hydrogen for the reaction was purified by passing through an oxygen trap. A glass reactor of 25-cm long and 1.0-cm diameter was used. The catalysts were used as prepared. A typical charge

of 0.2 g of catalyst was placed on a fine quartz wool bed supported on a sintered glass. The catalytic bed was about 2-mm thick and it has been checked that no external nor internal diffusion controlled the process. The temperature of the reaction was measured with a chromel–alumel thermocouple placed at the center of the catalytic bed. It was also checked, in the selected range of temperatures, that the reaction was not controlled by thermodynamics (the maximum conversion expected was 100%).

In a typical run the catalyst was reduced prior to reaction. It was heated in flowing H₂ (5 liter/h) at 773 K with a heating rate of 180 K · h⁻¹ and held 2 h at this temperature. The catalyst was then cooled to the reaction temperature in flowing H₂ and the gas mixture was passed over the cata-

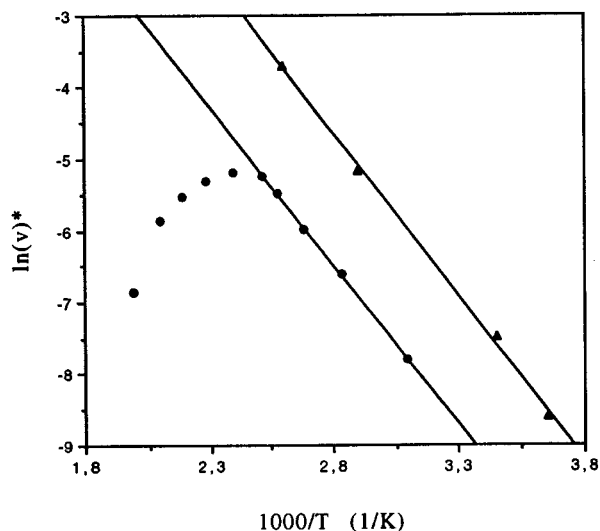


FIG. 1. Arrhenius plots showing the effect of temperature on the rate of benzene hydrogenation. Sample: Rh(Cl)/CeO₂ ER (0.33 wt% Rh); P_{C₆H₆} = 51.8 Torr and P_{H₂} = 708.2 Torr. For the sample Rh(Cl)/CeO₂ E reduced at 773 K (●), E_a = 37 kJ · mol⁻¹ between 323 and 388 K; for the sample Rh/SiO₂ reduced at 773 K (▲), E_a = 37.9 kJ · mol⁻¹. (Note. v is expressed in mol_{C₆H₁₂} · s⁻¹ · g_{Rh}⁻¹.)

lyst. Cyclohexane was the only product observed during the reaction.

Hydrogen chemisorption measurements were carried out at 313 K in a conventional high vacuum system equipped with a Datametrics capacitance gauge (type 1014 A). The standard procedure for reducing the catalysts consisted of heating the sample (0.2 g) in flowing H₂ (flow rate of 5 liter/h) at a heating rate of 180 K · h⁻¹ up to 773 K. The catalyst was held for 2 h at 773 K and further evacuated at 773 K for 1 h ($P \approx 10^{-5}$ Torr) in order to remove water and chemisorbed hydrogen species. The reactor was then cooled down to 313 K. The Sinfelt's "back-sorption" (23) method was used. According to this method, evacuation of the sample at the temperature of chemisorption eliminates reversible hydrogen without displacing the irreversible chemisorbed hydrogen. This method also assumes that no hydrogen was irreversibly adsorbed on the support. Thus hydrogen chemisorption measurements were realized by successive increases of hydrogen partial pressure over the catalytic bed until saturation of the metallic surface; at that time the total amount of hydrogen adsorbed (H_{Total}) was determined. Then the reactor was pumped off at 313 K until a high vacuum was reached and another series of hydrogen partial pressures was used to determine the amount of reversible hydrogen ($H_{\text{Reversible}}$). The amount of irreversible hydrogen ($H_{\text{Irreversible}}$) was calculated from

$$H_{\text{Irreversible}} = H_{\text{Total}} - H_{\text{Reversible}}. \quad [2]$$

The percentage of metal exposed was calculated by considering a stoichiometric adsorption of hydrogen over metallic rhodium (H/Rh ratio equal to unity) (19, 23, 24).

RESULTS

1. Catalyst Characterization

The main characteristics of the supports and catalysts are reported in Table 1. The ionic exchange was practically complete on the high surface area ceria (Rh(Cl)/CeO₂ E), whereas it only reached 50% on the low surface area calcined ceria (Rh(Cl)/CeO₂ CE). This relatively low yield was attributed to the calcination pretreatment which caused a drastic loss in specific surface area of CeO₂, as well as a strong dehydroxylation of the oxide surface. Both phenomena caused a strong decrease of the number of sites for exchange (hydroxyl groups) present on the surface of calcined ceria. Note as well that after calcination the specific surface area retained by the 144 m² · g⁻¹ ceria is higher when rhodium is present on its surface. CeO₂ C actually exhibits 6 m² · g⁻¹ after calcination at 1173 K, whereas Rh(Cl)/CeO₂ E exhibits 19 m² · g⁻¹ after calcination in the same conditions. Apparently, the presence of rhodium modifies the sintering of ceria support which results in a slight stabilisation of its surface area.

2. Benzene Hydrogenation

Since benzene hydrogenation is considered as a structure insensitive reaction over metallic rhodium, the turnover rate can be related to the number of catalytic sites by Eq. [1]. To calculate the number of accessible surface metallic sites (Rh(0)), we had to determine both the reaction and the turnover rate in the range of temperature used.

As the catalysts showed noticeable deactivation, the initial conversion could not be directly determined from its plot evolution versus time of run (Fig. 2a). The deactivation law for a catalyst proposed by Germain and Maurel (25) between the reciprocal value of the conversion versus time of run was used to determine the initial conversion (Eq. [3]). Fuentes and Figueras (21) and Maurel and Leclercq (26) have used this law to obtain initial conversions and rates.

$$\frac{1}{C} = \frac{1}{C_0} + a \cdot t \quad [3]$$

with

C , instantaneous conversion (%); C_0 , initial conversion; a , deactivation coefficient (s⁻¹); t , time (s).

For all catalysts the initial conversion was calculated by extrapolating this plot at $t = 0$ taking into account data over 100 min of run (Fig. 2b).

In order to check the origin of the deactivation process observed on all samples a temperature programmed desorption analysis was made on Rh(Cl)/CeO₂ ER after 150 min of benzene hydrogenation (Fig. 3). Desorption of benzene was shown and two peaks were observed. The first one, located at 360 K is associated with weakly adsorbed benzene, whereas the second one, located between 533 and 573 K, is associated with a stronger adsorbed benzene on Rh(0) particles. This strongly adsorbed benzene can progressively inhibit the active sites and cause the strong deactivation observed during benzene hydrogenation on the catalysts. This deactivation was observed on both Rh/SiO₂ and Rh/CeO₂ samples.

Figure 1 shows the effect of temperature on the rate of benzene hydrogenation. The curve obtained shows a maximum at 453 K indicating a change in the activation energy. This phenomenon has been observed by several authors (20, 27) and results in a change of order with respect to hydrogen and benzene partial pressures. Meerten and Coenen (27) attributed the drop of the reaction rate to a rapid decrease of the surface coverage of partially hydrogenated benzene molecules. Note that each point of the Arrhenius plot of Fig. 1 was obtained for a freshly reduced sample.

Several values of E_a and V_r are presented in the literature (19, 20, 28, 29) but, to our knowledge, none was determined over Rh/CeO₂. Since the reliable values of the percentages of metal exposed depend essentially on the

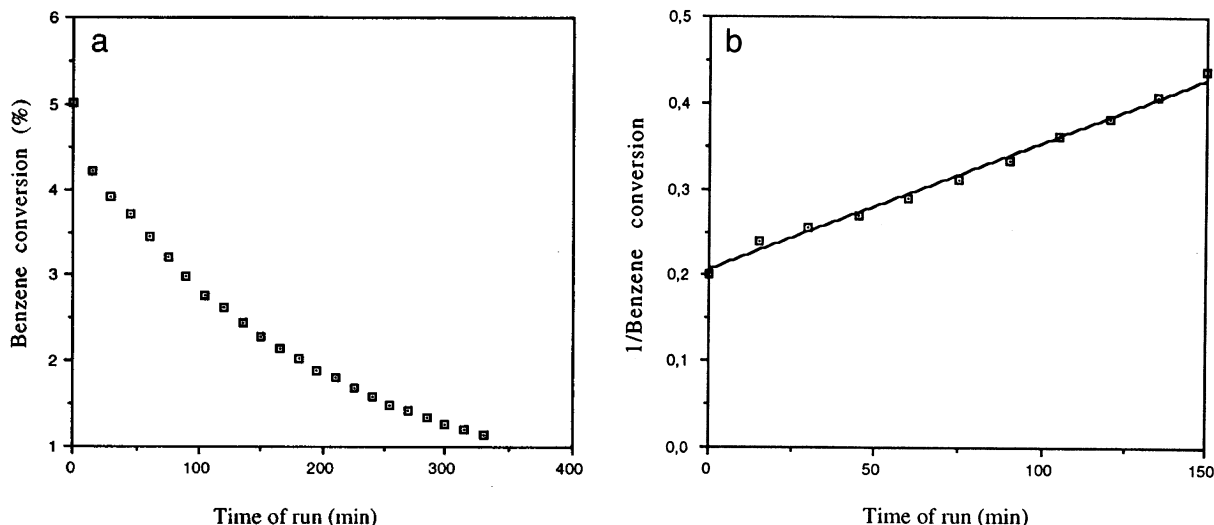


FIG. 2. Benzene hydrogenation over Rh(Cl)/CeO₂ ER: $T_r = 323$ K; $P_{C_6H_6} = 51.8$ Torr; $P_{H_2} = 708.2$ Torr; Weight of catalyst used = 200 mg. (a) Benzene conversion versus time of run. (b) Inverse of benzene conversion versus time of run.

accuracy of these two parameters, they should be determined on a Rh/CeO₂ catalyst.

Before calculating the percentages of metal exposed on reduced Rh(Cl)/CeO₂ catalyst, it was necessary to check that CeO₂ did not catalyze benzene hydrogenation. Lin and Vannice (30) have actually shown that, in some cases, the support itself could participate to benzene hydrogenation. In order to rule out this possibility, the activation energy of the reaction was calculated on Rh(Cl)/CeO₂ ER and compared to that of other systems (Rh/Al₂O₃ and Rh/SiO₂) containing rhodium as a unique metal phase but supported on different oxides. The value obtained for reduced Rh(Cl)/CeO₂ ER ($E_a = 37.0$ kJ · mol⁻¹) is in very good agreement with that found by Marques Da Cruz (20)

for Rh/Al₂O₃ (35.6 kJ · mol⁻¹). E_a was also determined on reduced Rh/SiO₂ prepared for this study ($E_a = 37.9$ kJ · mol⁻¹) and is also very close to that of Rh(Cl)/CeO₂ ER. Clearly, the good agreement existing between the activation energy of the three systems Rh/CeO₂, Rh/SiO₂, and Rh/Al₂O₃ showed that ceria did not participate in benzene hydrogenation.

The accuracy of the turnover rate depends on the reliability of the number of reduced accessible sites titrated by hydrogen chemisorption. In the case of the present Rh/CeO₂ catalysts, unreduced rhodium could not be excluded after reduction at 773 K, due to the low metal loading and to the low number of accessible Rh(0) measured by hydrogen chemisorption (Table 2). Taking into account that

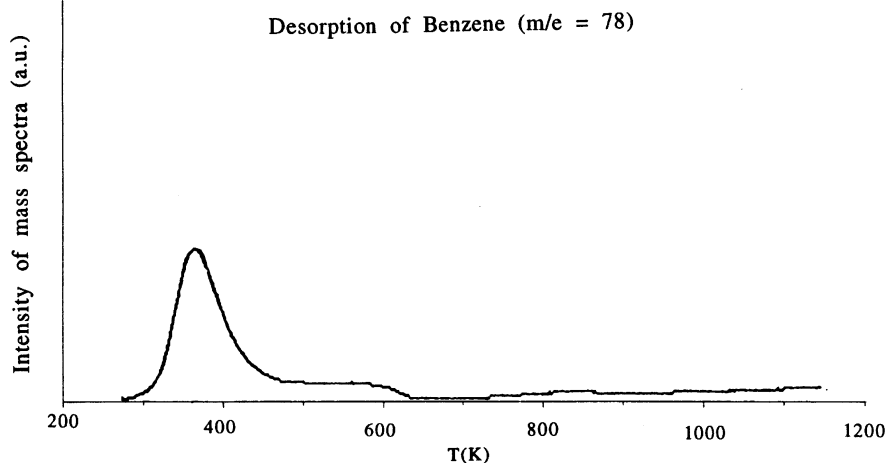


FIG. 3. TPD profile of benzene on Rh(Cl)/CeO₂ ER after benzene hydrogenation (7.5 K · min⁻¹).

TABLE 2

Benzene Hydrogenation and Hydrogen Chemisorption over Reduced Rh/SiO₂, Rh(Cl)/CeO₂ and Rh(N)/CeO₂ Catalysts

Catalysts ^a	Rh (wt%)	T _r ^b (K)	V _r ^c (s ⁻¹)	% Rh(0) exposed ^d	% Rh(0) exposed ^e
Rh(N)/CeO ₂ ER ^f	0.40	323	0.21	15.2	154.1
Rh(N)/CeO ₂ ER	0.40	323	0.21	12.3	33.4
Rh(Cl)/CeO ₂ ER ^f	0.33	323	0.21	21.0	21.0
Rh(Cl)/CeO ₂ ER	0.33	323	0.21	19.6	17.0
Rh(Cl)/CeO ₂ ER	0.33	353	0.68	20.4	17.0
Rh(Cl)/CeO ₂ ER	0.31	373	1.33	19.4	18.1
Rh(Cl)/CeO ₂ ER	0.31	388	2.11	20.4	18.1
Rh(Cl)/CeO ₂ ECR	0.33	373	1.33	5.3	4.3
Rh(Cl)/CeO ₂ CER	0.15	347	0.54	18.6	18.0
SiO ₂ IR	0.33	338	0.39	98.0	98.0

Note. P_{C₆H₆} = 51.8 Torr, P_{H₂} = 708.2 Torr, P_{total} = 760 Torr.

^a See Table 1 for nomenclature of E, I, C, and R.

^b Temperature of reaction (Kelvin).

^c Turnover rate (s⁻¹).

^d Percentage of metal exposed as calculated from benzene hydrogenation.

^e Percentage of metal exposed as calculated from hydrogen chemisorption.

^f Sample reduced at 573 K.

rhodium complexes can take up hydrogen (as for homogeneous catalysis (31)), the resulting hydrogen titration may have not been reliable enough to obtain a precise value of the turnover rate on Rh(0). Moreover, as discussed below, even if no large spillover of hydrogen is expected during chemisorption measurements on reduced Rh(Cl)/CeO₂ catalysts, a small contribution of this effect could not be excluded. Consequently, to minimize uncertainties on the turnover rate value, the calculation was made for a Rh/SiO₂ sample (H/Rh = 0.98, Table 2) for which rhodium was assumed to be fully reduced. In that case hydrogen spillover must exist but it is generally considered as completely reversible on the support.

The number of Rh(0) atoms present on 0.2 g of 0.33 wt% Rh/SiO₂ was evaluated by hydrogen chemisorption and benzene hydrogenation was carried out on the same weight of catalyst. The turnover rate was calculated at 338 K and the activation energy previously determined ($E_a = 37.9 \text{ kJ} \cdot \text{mol}^{-1}$) was used to extrapolate the turnover rate at 323 K for comparison with literature data. The turnover rate obtained (0.39 s⁻¹ at 338 K or 0.21 s⁻¹ at 323 K) was found to be in very good agreement with that currently presented in literature (0.22 s⁻¹ at 323 K).

Since it was shown above that ceria did not intervene in benzene hydrogenation and since this reaction is structure insensitive, the turnover rate determined for Rh/SiO₂ was considered as independent on the oxide support and was used to calculate the percentages of metal exposed for

Rh/CeO₂ catalysts. Turnover rates were extrapolated at the temperature of reaction using the activation energy determined over Rh(Cl)/CeO₂ ER.

Table 2 reports the percentages of metal exposed calculated from benzene hydrogenation on reduced Rh(Cl)/CeO₂ and Rh(N)/CeO₂ samples. Since the reliability of the values obtained depends on the accuracy of reaction rates and turnover frequencies, the aggregation of errors was estimated. To minimize the error made on the percentages of metal exposed, benzene hydrogenation should have been carried out at the same temperature than that used for the determination of the turnover rate on Rh(0) (338 K). In that case errors result only in the uncertainties made on the calculation of the turnover rate for Rh/SiO₂ (0.39 ± 0.02 at 338 K) as well as in the uncertainties inherent in the chromatographic analysis (3% (32)). In these conditions the maximum error made on the percentage of metal exposed was estimated to be within 8%. However, such a method should have demanded the determination of V_r for any temperature of reaction. Consequently it was preferred to use the turnover rate determined at 338 K on Rh/SiO₂ as a "reference" and to extrapolate its value for all temperature of reaction. In the latter conditions the use of the Arrhenius law to extrapolate the turnover rate implied higher uncertainties due to the contribution of the error made on the activation energy value. However, as the reference turnover rate was determined for a temperature (338 K) located between the upper and the lower temperatures of reaction used (respectively 323 and 388 K) additional errors were minimized. Errors were estimated to be within 8 and 10% of the values of the percentages of metal exposed. Experiments carried out on Rh(Cl)/CeO₂ ER for four different temperatures of reaction (323, 353, 373, and 388 K) showed that the calculated percentages of metal exposed were similar (relative variation of about 5%). This proved the reliability of the extrapolated turnover rates and in turn the accuracy of the activation energy determined on Rh(Cl)/CeO₂ ER.

Rh(0) particle sizes were calculated on reduced Rh(Cl)/CeO₂ catalysts from the percentages of metal exposed obtained from benzene hydrogenation (Table 3) and were compared to those obtained by HRTEM (18). The classical relation given in Eq. [4] was used (32):

$$d = f \cdot \frac{L \cdot V_{\text{Rh}}}{\% \text{ of metal exposed}} \quad [4]$$

with

- d , particle diameter (m)
- f , shape factor ($f = 6$ for a sphere)
- L , site density = $1.32 \times 10^{19} \text{ atoms} \cdot \text{m}^{-2}$
- $V_{\text{Rh}(0)}$, volume of a rhodium atom = $10.18 \times 10^{-30} \text{ m}^3$.

It was also assumed in these calculations that no rhodium atom was buried in the support after reduction. This

TABLE 3

Rhodium Particle Sizes of the Reduced Samples

	Rh(Cl)/CeO ₂ ER ^d	Rh(Cl)/CeO ₂ ECR	Rh(Cl)/CeO ₂ CER
% Rh(0) exposed ^b	20 ^c	5.3	18.6
<i>d</i> ₁ (nm) ^d	4.0	14.5	4.5
<i>d</i> ₂ (nm) ^e	≤5.0	≤7.5	≤5.0

Note. Calculated from the rates of benzene hydrogenation (*d*₁) and compared to those obtained by HRTEM (*d*₂).

^a See Table 1 for nomenclature.

^b Percentages of metal exposed as calculated by benzene hydrogenation.

^c Mean value calculated from the percentages of metal exposed obtained for CeO₂ ER samples (cf. Table 2).

^d Particle diameters calculated according to Eq. [4].

^e As explained in the Introduction, due to the limited number of Rh(0) particles observed for each sample and because larger aggregates should have been observed, the sizes measured were considered as upper values for the diameters of Rh(0) particles.

assumption was justified for Rh(Cl)/CeO₂ CER and Rh(Cl)/CeO₂ ER samples since small changes in the specific surface area of ceria were observed after reduction of the Rh(Cl)/CeO₂ CE and Rh(Cl)/CeO₂ E samples, respectively (Table 1). However, it did not apply to Rh(Cl)/CeO₂ ECR (the sample calcined and reduced after exchange), since the calcination step prior to reduction caused a strong sintering of the ceria support and could lead to a partial burial of the metal particles (18).

3. Hydrogen Chemisorption

Table 2 reports the percentages of exposed metal evaluated for Rh/SiO₂ and Rh/CeO₂ catalysts.

Note that the measurement of the number of metallic accessible sites on the sample Rh(Cl)/CeO₂ ECR could not be done with 0.2 g, due to the low number of Rh(0) exposed after calcination. The sample weight had to be increased up to 0.8 g to make measurable the amount of H₂ adsorbed. It is interesting to note that the percentage of metal exposed for this catalyst could be easily determined by benzene hydrogenation (5.3% of metal exposed) with only 0.1 g of sample.

Always, according to Table 2, it appears that the percentages of exposed metal evaluated by benzene hydrogenation and hydrogen chemisorption are in good agreement, except for the two Rh(N)/CeO₂ samples reduced at 573 and 773 K. For these catalysts the percentages of metal exposed were much larger than those determined by benzene hydrogenation. After reduction at 573 K the percentage of metal exposed was even larger than 100%. This strongly suggested that hydrogen spillover occurred during the chemisorption measurements of these two samples.

Typical isotherms obtained for both Rh(N)/CeO₂ and Rh(Cl)/CeO₂ reduced samples are shown in Fig. 4. The

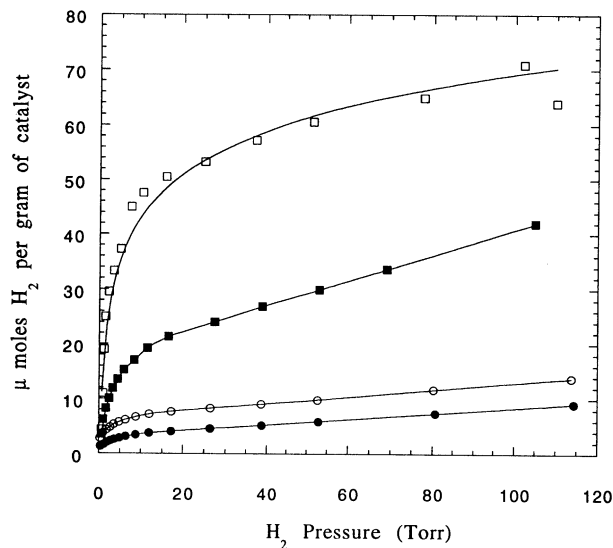


FIG. 4. Typical isotherms recorded during hydrogen chemisorption. On sample Rh(N)/CeO₂ reduced at 573 K: (□) H₂ total, (■) H₂ reversible. On sample Rh(Cl)/CeO₂ E reduced at 573 K, (○) H₂ total, (●) H₂ reversible.

shape of the isotherms recorded for Rh(N)/CeO₂ reduced at 573 K, compared to that recorded for Rh(Cl)/CeO₂ E reduced in the same conditions, suggests that slow processes took place when unchlorinated catalysts were put in contact with hydrogen. The strong drift observed with increasing the hydrogen pressure and the large H/Rh ratio (H/Rh ≈ 1.54) is consistent with the occurrence of hydrogen spillover from Rh(0) to reduced ceria. The large amount of reversible hydrogen indicates that reverse spillover of hydrogen occurred during the evacuation treatment following the recording of the first isotherm. The fact that both the total and reversible isotherms show similar and important drifts with increasing pressure also suggests that enough hydrogen was eliminated during the evacuation treatment at 313 K so that the spillover process could be again observed when the catalyst was put in contact with the second series of hydrogen partial pressures.

When chlorides were present on the catalyst, less hydrogen was chemisorbed and the drift with increasing pressure was almost negligible. This supports the fact that the presence of chlorine on Rh/CeO₂ systems inhibits the spillover process (10, 33). The contribution of reversible hydrogen despite the inhibition of the spillover process was attributed to the elimination of physisorbed hydrogen on ceria during the evacuation treatment following the first series of H₂ partial pressures.

DISCUSSION

In this study, benzene hydrogenation was used to evaluate the percentages of metal exposed of rhodium containing

catalysts with low commercial-like metal loadings (0.15 to 0.35 wt% of the oxide support).

To increase the sensitivity of benzene hydrogenation (higher turnover rate), temperatures between 323 and 388 K were selected. This also permitted the limitation of the deactivation process, attributed to an irreversible adsorption of benzene molecules on the metallic rhodium particles (Fig. 3). Considering the low metal loadings used, an increase of the contact time, by increasing the weight of catalyst, could not be done without involving problems of heat and mass transfers. Moreover, catalytic runs at temperatures higher than 388 K could not be done since above this temperature the activation energy was no longer constant (Fig. 1).

Low errors are expected when the percentages of metal exposed are calculated at the same temperature as that used for the determination of the turnover rate. For any other temperature of reaction, a reference turnover rate was determined at 338 K and then extrapolated by the Arrhenius law. Reactions carried out at 388, 353, 373, and 323 K on Rh(Cl)/CeO₂ ER showed that reliable percentages of exposed metal could be evaluated by this method (Table 2). The maximum error was estimated to be within 8 to 10% of the calculated percentages of metal exposed.

Benzene hydrogenation was carried out on reduced Rh(Cl)/CeO₂ and Rh(N)/CeO₂ samples. In both cases, the percentages of exposed metal showed small variation after reduction at 573 and 773 K. As suggested by Naccache *et al.* (34) for benzene hydrogenation over Pt/CeO₂ and Bernal *et al.* (8) for the same reaction over Rh/CeO₂, the influence of the reduction temperature on the catalytic activity seems to be rather small. Our results also indicate that no drastic SMSI effect occurred on our samples during the reduction treatment at 773 K.

Hydrogen chemisorptions were also carried out on the reduced Rh(Cl)/CeO₂ and Rh(N)/CeO₂ samples. The resulting percentages of exposed metal were compared to those obtained by benzene hydrogenation. As mentioned in the introduction, several studies concerning hydrogen chemisorption on Rh/CeO₂ showed that it was difficult to estimate the amount of hydrogen adsorbed on metal particles due to hydrogen spillover from the metal to reduced ceria. However, Bernal *et al.* (10) have shown that using rhodium chloride as precursor could result in a blocking of the spillover process, making possible accurate hydrogen chemisorption measurements at room temperature. Consequently, no hydrogen spillover was expected during hydrogen chemisorption carried out on Rh(Cl)/CeO₂ samples. This was confirmed since no overestimation of the percentages of metal exposed and no significant drift of isotherms with increasing hydrogen pressure were observed. As will be shown in a forthcoming paper (33), the absence of hydrogen spillover during chemisorption measurements can be attributed, in agreement with Bernal *et al.* (10), to the

substitution of the ceria lattice oxygen ions by Cl⁻ due to the use of RhCl₃ · 3H₂O as metallic precursor. The good correlation obtained between the percentages of exposed metal determined on reduced Rh(Cl)/CeO₂ catalysts by hydrogen chemisorption and benzene hydrogenation proves that both techniques count the same metallic sites (Rh(0)).

The case of sample Rh(Cl)/CeO₂ ECR showed that hydrogen chemisorption is not adapted to count the low number of metallic accessible sites (less than 5% of exposed metal) since 0.8 g were needed to make measurable the amount of hydrogen chemisorbed. In contrast, the percentage of exposed metal of this sample could be accurately determined by benzene hydrogenation with only 0.1 g of sample. This clearly shows that benzene hydrogenation is more sensitive than hydrogen chemisorption.

Unlike the case of reduced Rh(Cl)/CeO₂, the hydrogen chemisorption isotherms recorded for reduced Rh(N)/CeO₂ samples showed strong drifts with increasing hydrogen pressure. This phenomenon is typical of hydrogen spillover (4). The occurrence of hydrogen spillover left no doubt for the sample reduced at 573 K, since the percentage of metal exposed was overestimated (Table 2). Concerning the sample reduced at 773 K the percentage of metal exposed is lower than 100% (33.4%). This indicates that a *relative* inhibition of hydrogen spillover occurred when the temperature of reduction was increased from 573 to 773 K (4, 7, 8); however, the contribution of this process cannot be excluded. This phenomenon is attributed to the decrease in the number of OH groups which are believed to play an important role in the spillover mechanism.

Benzene hydrogenation was performed on both Rh(N)/CeO₂ samples reduced at 573 and 773 K. The percentages of exposed metal were close to those obtained for the Rh(Cl)/CeO₂ catalysts reduced at the same temperatures (573 and 773 K) and, as for the latter systems, they did not vary with the temperature of reduction. This suggests that the percentages of exposed metal determined from hydrogen chemisorption over Rh(N)/CeO₂ reduced at 573 and 773 K were both overestimated, due to hydrogen spillover. In contrast, benzene hydrogenation is not influenced by the hydrogen spillover occurring on the Rh(N)/CeO₂ catalysts. These results confirm that the use of hydrogen chemisorption to determine the percentages of exposed metal has severe limitations when hydrogen spillover occurs.

Benzene hydrogenation data were also used in the case of Rh(Cl)/CeO₂ samples to study the stability of the metal phase. The three catalysts (Rh(Cl)/CeO₂ ER, Rh(Cl)/CeO₂ CER, and Rh(Cl)/CeO₂ ECR) were reduced under the same conditions (2 h at 773 K in flowing H₂) but, in one case ceria was calcined prior to the exchange (Rh(Cl)/CeO₂ CER) and, in the other, the sample was calcined after the exchange (Rh(Cl)/CeO₂ ECR). Rh(Cl)/CeO₂ ER results from an exchange on the high specific surface area ceria prior to

reduction. The percentages of accessible metallic rhodium atoms determined by benzene hydrogenation were rather low (between 6 and 20%), and the corresponding metal particle sizes were compared to those determined by HRTEM (Table 3) (18).

Concerning Rh(Cl)/CeO₂ ER, no Rh(0) particles were observed by HRTEM, whereas particles sizes of 4.0 nm were deduced from benzene hydrogenation data assuming 100% reduction.

In the case of Rh(Cl)/CeO₂ ECR, particle sizes less than or equal to 7.5 nm can be expected from HRTEM results, whereas benzene hydrogenation predicts particle sizes of 14.5 nm. This discrepancy can be attributed to a partial burial of the metallic phase due to calcination after exchange. It follows an overestimation of the metal particle size when applying Eq. [4]. The burial of the metal phase is supported by the strong decrease of the percentage of metal exposed from 20%, in the case of Rh(Cl)/CeO₂ ER (no calcination after exchange), to 5.3%, in the case of Rh(Cl)/CeO₂ ECR (Rh(Cl)/CeO₂ E calcined and reduced), and by HRTEM which provided evidences for both burial and sintering of the metallic phase after calcination of Rh(Cl)/CeO₂ E (18). In fact, HRTEM measurements led to a percentage of exposed metal equal to 10.7%, whereas 5.3% is obtained theoretically from benzene hydrogenation. This indicates that 50% of the initial rhodium loading was buried in ceria during calcination.

The burial of the metallic phase observed for Rh(Cl)/CeO₂ ECR (18) is not surprising since it was supported on a high specific surface area support prior to calcination. Consequently, the calcination step caused a strong decrease in the specific surface area of the support (from 144 m² · g⁻¹ to 19 m² · g⁻¹) along with a partial burial of the metallic phase.

To avoid the burial of rhodium particles by support sintering, the high surface area support was calcined before the exchange, leading to the sample Rh(Cl)/CeO₂ CE. After reduction at 773 K, benzene hydrogenation calculations were in good agreement with HRTEM measurements (Table 3); both techniques indicate 5.0 nm rhodium particle sizes. Furthermore, the percentage of exposed metal was similar to that obtained after reduction of the high surface area sample, Rh(Cl)/CeO₂ E.

The question remains whether the metallic phase supported on a precalcined ceria support is more or less stable than that supported on a high surface area ceria. To check the stability of the metal phase on Rh(Cl)/CeO₂ CE, the sample was calcined once more and reduced at 773 K (Rh(Cl)/CeO₂ CECR sample). The percentage of metal exposed determined from benzene hydrogenation and the corresponding metal particle size were respectively 11.2% and 7.2 nm. To discuss the thermal stability of the metal phase on both Rh(Cl)/CeO₂ CE and Rh(Cl)/CeO₂ E, two points have to be considered: (i) 50% less rhodium was ex-

changed over the precalcined ceria support (0.15 wt%) compared to the high surface area ceria (0.33 wt%), (ii) 50% of the total rhodium loading of CeO₂ E (0.33 wt%) was buried into ceria after calcination of Rh(Cl)/CeO₂ E, whereas the totality of the rhodium loading on Rh(Cl)/CeO₂ CEC (0.15 wt%) remained at the surface after calcination.

From the preceding remarks it can be deduced that Rh(Cl)/CeO₂ CECR and Rh(Cl)/CeO₂ ECR retain on their surface similar amounts of rhodium. Considering the HRTEM percentage of metal exposed determined for Rh(Cl)/CeO₂ ECR (10.7%), it appears that Rh(Cl)/CeO₂ ECR and Rh(Cl)/CeO₂ CECR also expose similar amounts of metal rhodium atoms, respectively, 10.7% (from HRTEM) and 11.2% (from benzene hydrogenation). Hence, it may be interesting to first stabilize the specific surface area of the oxide support before depositing the metal phase on its surface.

CONCLUSION

Benzene hydrogenation and hydrogen chemisorption measurements were carried out on low loaded Rh/CeO₂ samples prepared from chlorinated (RhCl₃) and unchlorinated (Rh(NO₃)₃) precursors. It was found that benzene hydrogenation could lead to accurate evaluations of the number of metallic rhodium atoms exposed. The data obtained were in very good agreement with the percentages of metal exposed calculated from hydrogen chemisorption for Cl⁻ containing catalysts which showed that both techniques counted the same type of metallic sites (i.e., accessible Rh(0) atoms).

Unlike hydrogen chemisorption, benzene hydrogenation was not influenced by hydrogen spillover occurring over reduced unchlorinated catalysts and could still be used to evaluate accurate percentages of metal exposed. The high sensitivity of this technique makes it a good candidate for evaluating the percentage of metal exposed on low loaded commercial-like three-way catalysts. The following parameters were determined and used to count the number of metallic Rh atoms exposed: $Ea = 37.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $Vr = 0.21 \text{ s}^{-1}$ at 323 K.

In order to check the thermal stability of the metal phase, different catalysts were prepared. Rhodium was exchanged on both a high surface area ceria (144 m² · g⁻¹) and a low surface area ceria (6 m² · g⁻¹) obtained by calcination of the high surface ceria. A rhodium loading of 0.33 wt% could be achieved on the high surface area ceria whereas only 0.15 wt% could be obtained for the low surface ceria. Surprisingly, both catalysts exhibit the same amount of exposed metal rhodium atoms after calcination at 1173 K and reduction at 773 K. The advantage of depositing the metal phase on a precalcined support is that the total amount of the metal loading remains at the surface of the oxide support after calcination, whereas a large part is lost by burial into

the oxide support (about 50%) when rhodium is supported over a high surface area ceria before calcination. However, in that case, the amount of rhodium exchanged is limited by the low surface area of the sample. Hence, to optimize the process it would be interesting to apply this procedure to oxide supports capable of retaining higher specific surface areas after calcination.

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