JOURNAL OF CATALYSIS **166,** 229–235 (1997)
ARTICLE NO. CA971493

Characterization of Model Three-Way Catalysts

I. Determination of the Accessible Metallic Area by Cyclohexane Aromatization Activity Measurements

Eric Rogemond,* Nadine Essayem,† Roger Frety,* Vincent Perrichon,*,[1] Michel Primet,* and F. Mathis‡

**Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634 CNRS/UCB Lyon I, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France; †Institut de Recherches sur la Catalyse, 2 Avenue Einstein, 69626 Villeurbanne Cedex, France; and ‡Régie Nationale des Usines Renault, Direction de la Recherche, 67 Rue des Bons-Raisins, 92508 Rueil-Malmaison Cedex, France*

Received April 18, 1996; revised July 2, 1996; accepted October 14, 1996

The accessible metallic area measured by hydrogen chemisorption on model ceria–alumina supported platinum or(and) rhodium catalysts has been compared to the results obtained in cyclohexane aromatization activity tests. The benzene formation was studied at 573 K after reduction by hydrogen at the same temperature. The turnover frequency, calculated on the basis of hydrogen chemisorption data, was found to depend on the type of support, ceria or alumina, in interaction with the precious metal particles. However, for the catalysts supported on ceria–alumina, the activity per metallic platinum or rhodium site was almost the same for both fresh catalysts or after hydrothermal aging at 1273 K. The possible use of the cyclohexane aromatization activity measurement for the determination of the metallic area of three-way catalysts is examined. Compared to hydrogen chemisorption, this method presents the advantage of a better sensitivity for measuring very low dispersions of aged catalysts, typically dispersions inferior to 3%. In the discussion, the possible influence of hydrogen spill-over effects and of the connected role of chlorine are considered. Although not directly studied, the possible effect of sulphur present in commercial catalysts aged in vehicles is also discussed.

1. INTRODUCTION

Accessible metallic area is an important parameter for the characterization of supported metal catalysts. It is generally referred to as the metallic dispersion. Most of the time, this property is quoted as H/M since the classical method of measurement is the irreversible hydrogen chemisorption performed at room temperature, each superficial metal atom adsorbing a determined number of hydrogen atoms (1). Subsequent titration by gaseous hydrogen of the oxygen uptake is sometimes used for the same measurements, especially in the case of platinum catalysts for which the hydrogen amount mobilized for oxygen titration is three times higher than direct hydrogen adsorption (2, 3). Other adsorbates can be used, as well as certain physical methods. In this respect, high resolution transmission electron microscopy may give good imaging of the particles. X-ray diffraction line-broadening analysis permits the measurement of the mean crystallite diameter of the metallic particles and, when possible, is used to check the validity of the hydrogen chemisorption data.

However, these physical methods are not always usable, especially in the case of the three-way catalysts for which the metallic content is very low (precious metal concentrations close to 0.1–0.5%) and where the presence of cerium oxide prevents the direct microscopic observation of the metal particles because of a lack of contrast with the support. For such systems, the hydrogen chemisorption measured by volumetric techniques remains the base method, but it has to face two major problems.

The first is related to the presence of CeO_2 in the support. Indeed, hydrogen spillover was found to occur very easily on the ceria support at room temperature for a number of M/CeO_2 catalysts (4, 5). It can lead to hydrogen migration on the support, resulting in a higher hydrogen uptake which invalidates the dispersion measurement. Sometimes, this difficulty can be minimized. In particular, in the presence of chlorine, the spillover process is inhibited which allows the measurement of the accessible metallic area (6). This is the case when the catalysts are prepared from chlorinated precursors (7), but it may not be verified for catalysts of unknown origin. In addition, since ceria is a reducible oxide and contributes to oxygen storage (8), it does not seem possible to use gaseous oxygen titration to check the dispersion of the metals.

The second problem is that, due to the low content of precious metals, a high sensitivity of the hydrogen chemisorption measurement is required to obtain a good estimate of the metal dispersion. This is particularly critical for aged catalysts which have been submitted to high temperature treatments.

---

[1] To whom correspondence should be addressed.

0021-9517/97 $25.00

In previous work, related to the characterization of three-way catalysts (7), we prepared several model platinum and rhodium catalysts supported on alumina and ceria–alumina and studied the influence of the reduction temperature on the metal accessibility measured by hydrogen chemisorption. The hydrogen-atom/metal ratio (H/M) was found to be maximum when the catalysts were previously reduced at 573 K. In the case of platinum/ceria–alumina catalysts, we were able to validate the obtained values by FTIR spectroscopy of adsorbed CO. That was not possible on the rhodium catalysts due to the multiple modes of adsorbed CO on rhodium. The objective of the present work is to study the catalytic behaviour of the same type of ceria–alumina supported Pt or Rh catalysts in a "structure insensitive reaction" in order to assess whether the activity measurement is able to lead to an accessible metal area which is comparable to the value deduced from hydrogen chemisorption. The cyclohexane dehydrogenation into benzene, or cyclohexane aromatization, was chosen because this reaction was already used to determine the free metal surface of the noble metal catalysts (9–11). This reaction was preferred to the direct hydrogenation of benzene since it is performed at higher temperature, 550–600 K, instead of 275–300 K. It has the advantage of being more representative of the temperature range used during the three-way catalysis, without inducing modifications of the metallic surface during catalysis or strong metal-support interaction (SMSI) effects (12, 13). This reaction is considered as structure insensitive in the case of supported metal catalysts (14–18) and it was observed that the activity can change with the support (19). However, a certain degree of sensitivity to surface structure has been found for platinum single-crystal surfaces, but it is not clear why a difference with supported platinum catalysts exists (20, 21). Considering the bimetallic systems, we have applied this reaction to our model Pt and Rh systems, with the initial idea that a large difference in the turnover frequency of the two metals could allow us to estimate the surface composition of bimetallic systems. In fact, the results have shown that, on ceria–alumina, the activity per metallic site is the same for platinum and rhodium. Consequently, by measuring the catalytic activity, it becomes possible to determine the metallic area of Pt–Rh three-way catalysts. The interest of this method is illustrated by measurements on aged catalysts, i.e., on the same catalysts after hydrothermal treatment at 1273 K.

2. METHODS

2.1. *Catalyst Preparation*

The monometallic catalysts are those previously studied (7). The alumina support (Al) was a SCM129 Rhône-Poulenc material with a 107 m^2g^{-1} BET area. The ceria–alumina support (CeAl) was prepared by successive reactions of $Ce(acac)_3$ in a toluene solution with the hydroxyl groups of the alumina surface. After drying under vacuum at 373 K, the solid was further calcined at 673 K (22). The ceria content was 21.9 wt% and the resulting specific surface area was 110 m^2g^{-1}.

TABLE 1

Chemical Analyses (wt%) and Specific Surface Areas of the Catalysts

Catalyst	Pt (wt%)	Rh (wt%)	Ce (wt%)	S_{BET} (m^2g^{-1})
0.5Pt/Al	0.57			110
0.5Pt/CeAl	0.59		18.9	107
0.5Rh/Al		0.46		109
0.5Rh/CeAl		0.45	19.4	109
1.0Pt-0.2Rh/Al	1.0	0.15		105
1.0Pt 0.2Rh/CeAl	1.13	0.19	19.3	104

These two supports were impregnated with aqueous solutions of H_2PtCl_6 or $RhCl_3$ in order to obtain four monometallic samples: 0.5 wt% Pt/Al, 0.5 wt% Rh/Al, 0.5 wt% Pt/CeAl, 0.5 wt% Rh/CeAl and two bimetallic systems (1.0 wt% Pt + 0.2 wt% Rh)/Al or /CeAl. After drying for one night at 383 K, they were treated for 2 h at 773 K under nitrogen flux. The noble metal loading and the cerium content, determined by atomic emission spectroscopy, and the specific surface area are given in Table 1. The latter, between 104 and 110 m^2g^{-1}, can be considered constant.

These catalysts were tested as prepared and after hydrothermal aging at 1273 K. The aging was performed for 5 h on a few grams of catalyst deposit on a quartz frit using a 6 l h^{-1} flow of $N_2 + 10\%\ H_2O$. Water was introduced into the gas flow with an automated syringe.

2.2. *Hydrogen Chemisorption Measurements*

Hydrogen chemisorption was measured at room temperature, in static conditions, with a conventional glass volumetric setup according to a procedure already described which included 1 h evacuation of the sample at 723 K and a reduction overnight at 573 K (7). The back-sorption method was used (23), the amounts of total and reversible hydrogen uptakes being obtained by extrapolating the quasi-linear portions (0–15 mbar) of the isotherm to zero pressure. The difference between the two values gave the amount of irreversible hydrogen uptake, from which the number of accessible metallic atoms was deduced, assuming a stoichiometry of one hydrogen atom per surface metal atom (1, 2, 24).

2.3. *Rate Measurement in the Cyclohexane Aromatization*

The catalytic activity measurements were performed at 573 K in a differential flow microreactor, using a 10 mg sample. For aged catalysts, the mass was increased to 90 mg. The reaction mixture ($P_{H_2} = 0.93$ bar, $P_{Cyc} = 0.07$ bar) was obtained by flowing hydrogen in a cyclohexane saturator kept at 285 K. Although conversion was unfavoured by a high initial H_2 pressure, the presence of hydrogen was necessary to preserve the metallic state and inhibit the formation of carbon deposits (9–11). The total flow rate was 7.8 l h^{-1}. In these conditions, 573 K was the optimal temperature in order to obtain a sufficient conversion without reaching the thermodynamic limitation (80% at 573 K). The analysis of products was performed by gas chromatography (FID detector) after separation in a Carbowax 20M column.

3. RESULTS

3.1. *Determination of the Metallic Area by Hydrogen Chemisorption*

Table 2 gives the changes in the accessible metallic area H/M for each of the prepared solids. The method applied for the monometallic systems (7) was extended to the bimetallic catalysts. The equivalent dispersion value (H/M) for the catalyst 0.5 Pt/CeAl was verified using FTIR spectroscopy of CO adsorbed specifically on the metallic surface (26). By assuming the 1CO/1M stoichiometry, the corresponding H/M value was 51%, which is close although slightly smaller than that deduced from H_2 chemisorption (59%).

In the case of the bimetallic catalyst, the dispersion is calculated by supposing the adsorption to be independent of the nature of the metallic adsorbent but always keeping the stoichiometry 1H/1M. The metallic dispersion varies with the support. On alumina, H/M is equal to 60%, whereas on ceria–alumina it is 37%. Although the atomic ratio Pt/Rh is almost 2.5 in this solid, the latter value is closer to the dispersion obtained in the case of the rhodium systems.

3.2. *Cyclohexane Aromatization Reaction*

Prior to the test, the catalysts were reduced by hydrogen for 5 h at 573 K, and then reactants were admitted at the same temperature. On the supports alone (alumina or ceria–alumina), no activity could be measured at 573 K. For the supported metal catalysts, the activity decreased during the first hours of reaction, at least for rhodium systems, as is illustrated in Fig. 1. To compare the activity data between the catalysts and to avoid any major modification of the surface, it is necessary to consider the initial activity before significant deactivation occurs. For practical reasons due to reactor dead volume and for better reproducibility, the initial conversion was taken as that measured after 10 min. In these conditions, the precision of the measurements was between 10 and 20%. No hydrogenolysis or reaction product other than benzene was detected in our experimental conditions and the carbon balance was almost 100%. The values of conversion were usually lower than 15%, with a few exceptions, as for example the case of the 0.5Pt/Al catalyst with a conversion of 29%, as shown in Fig. 1. A priori, this value is a little high to be considered differential. However, in this case, the Arrhenius plot obtained between 541 and 573 K (conversion between 13.7 and 29.2%) was found to be linear, the absence of curvature indicating that diffusion was not rate-determining.

TABLE 2

Accessible Metallic Area (H/M) after Reduction at 573 K

Catalyst	H/M (%)
0.5Pt/Al	68
0.5Pt/CeAl	59(51)[a]
0.5Rh/Al	33
0.5Rh/CeAl	37
1.0Pt 0.2Rh/Al	60
1.0Pt 0.2Rh/CeAl	37

[a] Deduced from FTIR spectra of adsorbed CO.

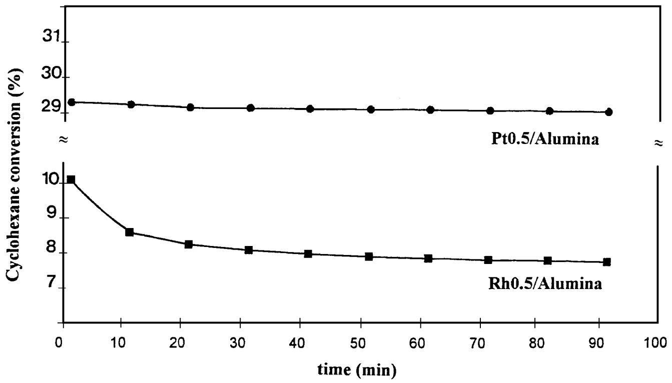

FIG. 1. Cyclohexane conversion vs time for platinum or rhodium on alumina catalysts: reaction temperature is 573 K, $P_{H2} = 0.93$ bar, $P_{Cyc} = 0.07$ bar, and flow rate is 7.8 l h^{-1} for 10 mg catalyst.

The values of the initial activity are given in Table 3. They are calculated per gram of metal and also per metallic site (turnover frequency, TOF), using the metallic area determined by hydrogen chemisorption.

On alumina, the platinum turnover frequency at 573 K is around two times higher than that of rhodium, whereas for the bimetallic Pt–Rh, the TOF is closer to that of the monometallic rhodium catalyst. The same observations are also valid at 543 K, the temperature chosen for comparison with the literature. At this temperature, the TOF for platinum is in rather close keeping with that determined by Hoyos *et al.*, 15×10^3 instead of 11.5×10^3 h^{-1} (25), in agreement with previous results (9). However, in the case of rhodium, the catalyst of the present study is much more active than the rhodium/alumina catalyst studied by Hoyos *et al.* (25), with a TOF value of 6.2×10^3 instead of 1.2×10^3 h^{-1}.

In contrast to alumina, on a ceria–alumina support the turnover frequencies are almost the same for the

TABLE 3

Activity and Turnover Frequency of the Catalysts Supported on Alumina or Ceria–Alumina in the Cyclohexane Aromatization Reaction at 543 and 573 K

Catalyst	T_{reaction} (K)	Activity ($\text{mol} \cdot \text{h}^{-1}\text{g}_{\text{met}}^{-1}$)	H/M (%)	TOF (10^3 h^{-1})
0.5Pt/Al	573	109	68	32
	543	51		15
0.5Rh/Al	573	42	33	13
	543	20		6.2
1.0Pt 0.2Rh/Al	573	60	60	17
	543	26		7.5
0.5Pt/CeAl	573	44	59	15
0.5Rh/CeAl	573	54	37	15
1.0Pt 0.2Rh/CeAl	573	34	37	16

monometallic rhodium and platinum catalysts and also for the bimetallic solids. The deviation between the three solids is within the experimental error and the average TOF at 573 K can be established as equal to 15×10^3 h^{-1}.

It is justifiable to attribute this constancy to the presence of ceria in the support. However, it is necessary to confirm this effect on another specimen. For this purpose, we prepared a new platinum catalyst deposited on the same ceria–alumina support (2 wt% Pt) in order to modify the relative proportion of the platinum atoms in contact with the ceria support. This 2Pt/CeAl had a metal content four times higher. The metallic dispersion obtained by hydrogen chemisorption was 36%. The corresponding TOF was found to be equal to 14×10^3 h^{-1}, which is almost the same as that of the less loaded catalyst (15×10^3 h^{-1}). This means that the activity of one platinum site is the same, independent of the coverage of the ceria surface by platinum. In other words, the ceria surface as a whole does not seem to be involved in the reaction mechanism. If ceria sites intervene in the reaction, only the oxygen ions and the anionic vacancies created by the reduction at 573 K and located close to the metallic particles can be involved in the mechanism.

The fact that for the ceria–alumina support no difference of turnover frequency is found between platinum and rhodium, unlike the case of the alumina support, was unexpected. It was interesting to see whether it could be generalized to aged solids with a much lower metallic dispersion. In the next section, we examine the results obtained with the same catalysts after aging at 1273 K.

3.3. *Influence of Aging on the Hydrogen Chemisorption and Catalytic Properties*

Thermal aging at high temperature is a key factor in the lifetime of three-way catalysts, because metal sintering can be considered as primarily responsible for the loss of catalytic activity. Therefore, it is important to determine the accessible metal area after such a deactivation and we have applied the two previous methods to the same ceria–alumina supported catalysts subjected to high temperature treatment. In a catalytic muffler, the catalyst is submitted alternately to rich and lean conditions, and the average water content oscillates around 10–12 vol%. The sintering of the metallic particles is generally considered as more severe in a lean mixture, whereas that of ceria will occur more readily in a rich mixture. However, water vapour is also well known to favour extensive sintering. Therefore we have chosen to treat the samples hydrothermally at 1273 K which is a temperature high enough to induce significant sintering. Thus, the aging was done on the solids reduced by hydrogen at 773 K by heating them for 5 h at 1273 K under a mixture of $N_2 + 10\%$ H_2O.

The aged solids were first studied in hydrogen chemisorption at 294 K. A steep decrease of the irreversibly adsorbed hydrogen quantities was observed. For the lowest adsorption values, the H_2 quantities were close to the method sensitivity limit (around 0.3 μmol H_2 per gram of catalyst). The corresponding metallic areas, expressed as dispersion H/M, are given in Table 4. For the highly loaded platinum catalyst, the dispersion diminishes to 10%. For the two other solids, the calculated dispersions are very low, 1.7 and 2.6%. These two values are within the sensitivity limit of the method and it is difficult to establish with certainty which is the more "dispersed"solid.

The same solids were studied in the cyclohexane aromatization reaction. For the less dispersed solids, the sample mass was increased to 90 mg. In these conditions, the cyclohexane conversion is high enough (8–18%) to obtain activity values with a high degree of reliability. The turnover frequencies calculated on the basis of the hydrogen chemisorption are also given in Table 4.

The turnover frequencies are of the same order of magnitude as those of the fresh catalysts. It is lower for platinum than for rhodium, which is itself close to that of the bimetallic system. Since the TOFs are calculated using dispersion values which are low and obtained with poor precision, the relative error may be very important.

TABLE 4

Hydrogen Chemisorption and Cyclohexane Aromatization Activity at 573 K

Catalyst after Aging at 1273 K	H/M (%)	Sample Mass (mg)	Conversion (%)	Activity ($\text{mol} \cdot \text{h}^{-1}\text{g}_{\text{met}}^{-1}$)	TOF (10^3 h^{-1})
2Pt/CeAl	10	10	5.9	6.4	13
0.5Rh/CeAl	1.7	90	8.2	4.0	24
1.0Pt 0.2Rh/CeAl	2.6	90	18.4	3.4	23

3.4. Relationship between Cyclohexane Aromatization Activity and Hydrogen Chemisorption for the Ceria–Alumina Catalysts

Figure 2 shows the activity in the cyclohexane aromatization at 573 K, expressed per gram of metal, as a function of the quantity of hydrogen chemisorbed at 298 K. A linear relationship is observed, including fresh or aged catalysts, i.e., high and low dispersions. The value of the slope is 30 mol h^{-1} of cyclohexane transformed per 1 mmol of hydrogen. Keeping the assumption of one hydrogen atom adsorbed per metallic site, this corresponds to a turnover frequency of $15 \times 10^3\ h^{-1}$, which is close to the values given in Tables 3 and 4.

The existence of the linear relation shown in Fig. 2 allows us to deduce that the measurement of the activity at 573 K in the cyclohexane dehydrogenation can be considered as a new tool for determining the number of precious metal atoms present at the surface of ceria–alumina supported catalysts. In other words, it may constitute a technique for a direct measurement of the metallic dispersion. For the ceria–alumina support, this is verified whether the deposited metal is platinum or rhodium. This is not the case for alumina as the support, for which the TOF depends on the metal.

The reciprocal way to take advantage of the linear relationship of Fig. 2 is to use the calibration turnover frequency ($\mathrm{TOF} = 15 \times 10^3\ h^{-1}$) in order to calculate the metallic dispersion D_{cyclo} for the series of catalysts, independent of hydrogen chemisorption. Table 5 compares the data obtained with those of hydrogen chemisorption D_{H}. The dispersions D correspond to M_s/M, the ratio of the number of surface metal atoms to the total number of metallic atoms.

It is logical that the dispersion values in columns 2 and 3 are very close. When the dispersion is very low, the degree of confidence is certainly better for D_{cyclo} because, as mentioned above, the sensitivity in collecting the activity data is higher than for hydrogen adsorption measurements.

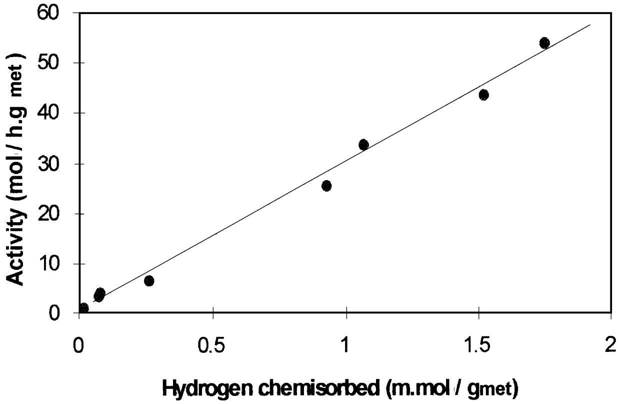

FIG. 2. Cyclohexane aromatization activity at 573 K vs hydrogen chemisorbed at 298 K for ceria–alumina supported catalysts.

TABLE 5

Application of the Cyclohexane Aromatization Reaction to the Determination of the Metallic Dispersion

Catalyst	D_{H}[a] (%)	D_{cyclo}[b] (%)	Mean Particle Size (nm)
Fresh			
0.5Pt/CeAl	60	57	2.0
2Pt/CeAl	36	33	3.5
0.5Rh/CeAl	38	37	2.7
1.0Pt 0.2Rh/CeAl	37	39	2.7
After aging at 1273 K			
2Pt/CeAl	10	8	14
0.5Rh/CeAl	1.7	2.7	37
1.0Pt 0.2Rh/CeAl	2.6	3.9	27

[a] Hydrogen chemisorption at 298 K.
[b] Cyclohexane reaction temperature = 573 K.

The mean metal particle sizes d deduced from D_{cyclo} are also given in Table 5. They were obtained by supposing the absence of encapsulation and assuming spherical or cubic particles according to the classical formula

$$d = 6(v_{\mathrm{m}}/a_{\mathrm{m}})/D,$$

where v_{m} and a_{m} represent the volume and the surface area occupied by a metallic atom according to the standard data (30). These values illustrate the important sintering of the metallic particles. The catalyst containing 2 wt% platinum appears to resist sintering better than the systems with a lower metal loading. The interpretation is not straightforward. However, the fact can be considered as well established since two independent methods lead to this result. This could suggest that for lower metal content, high temperature treatments may result in burial of the metal in the ceria support, resulting from the migration of the metal in a surface vacancy toward a bulk vacancy, according to the model developed by Sanchez and Gazquez (12). In the case of higher metal loadings, a higher proportion of the metal atoms would remain dispersed on the surface. Finally, for rhodium, one may also consider that interactions with the alumina support could allow formation of rhodium ions not reducible by hydrogen at 573 K.

4. DISCUSSION

The results presented above show that the hydrogen chemisorption and the cyclohexane aromatization methods give the same metallic area when platinum or/and rhodium are supported on ceria–alumina. The fact that the TOF is the same for platinum and rhodium when cerium oxide was present and not for the same metals when supported on alumina can only mean that the intrinsic properties of each metal are hidden by the action of reduced ceria.

A possible general interpretation would be that reduced ceria deeply modifies the electron density of the metal atoms, thus changing the adsorption energies and the coverage of the adsorbed species. However, there is no reason why the properties for rhodium and platinum become the same and there is no evidence to support this model.

If metallic atoms are not involved in the rate-determining step, this observation can be attributed to the intervention of ceria in the reaction mechanism. One can suppose that ceria–alumina support which alone is totally inactive may intervene, in the presence of a metal, in the reaction steps. The global reaction is

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2.$$

This may be viewed as occurring via a series of consecutive dehydrogenation steps. In the first step, the cyclohexane has to be dissociatively adsorbed on the metal with formation of a bond between hydrogen and metal atoms. The successive dehydrogenation steps eliminate three hydrogen molecules through processes which require several sites. If such sites are also available on the support as temporary hydrogen storage sites, the intervention of the support may favour the elimination of hydrogen. However, the TOF value for platinum is lower on ceria–alumina than on alumina, which means that alumina would be more favourable to this hydrogen transfer than ceria. This is surprising, because one would expect good hydrogen mobility on the ceria surface. A possible interpretation of this observation is that hydrogen spillover and reverse spillover phenomena are strongly inhibited when the concentration of surface oxygen ions is decreased (5, 27). Indeed, the 573 K reduction treatment performed before the catalytic test is sufficient to create surface oxygen vacancies on the ceria surface with formation of Ce^{3+} ions on the whole surface extent (5, 28, 29). In these conditions, the highly reduced surface inhibits the hydrogen mobility and the possible transfers between the metal and the support. To be valid, this interpretation should also explain the results for rhodium, since these spillover phenomena were basically observed for rhodium supported on ceria. However, the inhibiting effect of the reduced ceria on the dehydrogenation step was not observed when ceria is added in the support for 0.5Rh/Al and 1.0Pt 0.2Rh/CeAl. Therefore, another explanation must be sought.

Another parameter which may be involved in the mechanism is the possible effect of chlorine ions. It has been shown previously (6) that the presence of Cl^- inhibited the direct and back hydrogen spillover processes. A chemical analysis performed on 0.5Pt/Al and a similar new 0.5Pt/CeAl sample indicates that respectively 75 and 96% of the chlorine introduced on the support with H_2PtCl_6 are still present after calcination at 773 K. For 0.5Rh/CeAl, all the chlorine remains in the solid (107% of the theoretical value). Thus it appears that when ceria is present more chlorine is present on the support. However, this change in the chlorine content does not seem significant enough to explain the difference between the alumina and ceria–alumina catalysts. Moreover, the literature indicates that chlorine has a limited effect on the kinetics of cyclohexane-type hydrocarbon dehydrogenation. Thus Rochefort [31] did not observe a significant activity increase in the presence of chlorine on 0.5% $Pt/\alpha Al_2O_3$ catalysts. Similarly, Guénin *et al.* (9) found that chlorine modifies the reaction kinetics very little. El Hazhar [32] studied the influence of direct addition of chlorine (as CH_2Cl_2) in the reacting mixture and found it positive when platinum was deposited on a basic support but slightly negative if the support acidity increases. In fact, the activity change was only temporary, which would indicate the very low influence of chlorine and the permanence of the active area. Thus it can be concluded that the preceding results on Pt and Rh supported on alumina or ceria–alumina cannot be directly related to the presence of chlorine. More studies are necessary to understand the origins of these effects.

Finally, an important point to discuss is whether cyclohexane aromatization can be used as a probe reaction for measuring the metallic area of real there-way catalysts after aging under vehicle conditions. The main problem associated with such materials is the great number and variety of components of the initial system and the large content of deposited poisons. In particular, there is a significant concentration of sulphur present due to the buildup of sulphates on the washcoat. Under reducing conditions, this sulphur should be reduced to sulphide species which by adsorbing on the metallic particles will probably lower the cyclohexane aromatization rate as they suppress the adsorption of hydrogen and therefore decrease the true metallic dispersion. For example, such sulphur poisoning on this reaction was evidenced on palladium-based catalysts [25]. However, in the absence of experimental data in the presence of sulphur, which was not the purpose of this paper, it should be noted that, for both the hydrogen chemisorption and the aromatization test, we have prereduced our catalysts at 573 K, which was found to be the most suitable pretreatment to give the maximum metal accessibility. This was particularly shown in Ref. (7) for commercial catalysts containing around 0.4–0.5% sulphur and also for the 0.5Pt/CeAl catalyst containing 0.46% sulphur, introduced as $BaSO_4$ by mixing with the support. Compared to the catalyst without sulphur, for which the reduction at temperatures higher than 623 K resulted in a lower metal accessibility due to strong interactions between platinum and ceria, the presence of $BaSO_4$ accelerated the loss of metallic area. Under these conditions, one can suppose that, by keeping the reduction temperature at 573 K and also limiting the reaction temperature at the same value, the detrimental sulphur effects will remain limited and not be more detrimental than for hydrogen chemisorption. Under these conditions, the cyclohexane aromatization could be a possible method to measure the metallic dispersions of aged catalysts with a higher degree of accuracy than with hydrogen chemisorption because of the better sensitivity of the reaction technique.

5. CONCLUSION

The dehydrogenation of cyclohexane into benzene was studied on various Pt and(or) Rh deposited on alumina and ceria–alumina supports. The aromatization activity has been found to depend on the metal when supported on alumina. In contrast, on ceria–alumina supports, the turnover frequency is independent of the nature of the metal. This constancy has been attributed to the presence of ceria.

Consequently, the application of this reaction to the determination of metallic dispersion is quite possible, provided that a preliminary calibration is realized. The dispersions obtained are the same as those derived from the classical method of irreversible hydrogen chemisorption. However, it has the advantage of being more sensitive for dispersions smaller than a few percent. This higher sensitivity can be very useful when studying catalysts aged at high temperature. Hence this technique can advantageously be proposed for studying the automotive three-way catalysts and the changes of the metallic dispersion incurred during their lifetime, from the initial state to highly damaged states. However, in this case, other parameters may interfere in the reaction, in particular the susceptibility of the sulphate content to be reduced under hydrogen into sulphide species which then could irreversibly poison the metallic sites. These detrimental effects can be limited if the reduction and the reaction temperatures are maintained equal to 573 K.

The extension of this method to monometallic systems deposited on other supports requires more data. It is probably not relevant for other bimetallic catalysts insofar as the constancy of the turnover frequency observed with ceria–alumina supports could be due to the intrinsic properties of ceria. More studies are required for a better understanding of the origin of this effect.

ACKNOWLEDGMENTS

Renault S. A. is gratefully acknowledged for financial support of this work through Contract 820554. The authors are also indebted to Mrs. M. Chevrier and C. Gauthier for helpful discussions.

REFERENCES

1. Scholten, J. J. F., Pijpers, A. P., and Hustings, A. M. L., *Catal. Rev. Sci. Eng.* **27**, 151 (1985).
2. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 705 (1965).
3. Suh, D. J., Park, T. J., and Ihm, S. K., *J. Catal.* **149**, 486 (1994).
4. Miller, J. T., Meyers, B. L., Modica, F. S., Lane, G. S., Vaarkamp, M., and Koningsberger, D. C., *J. Catal.* **143**, 395 (1993)
5. Bernal, S., Calvino, J. J., Cifredo, G. A., Rodriguez-Izquierdo, J. M., Perrichon, V., and Laachir, A., *J. Catal.* **137**, 1 (1992).
6. Bernal, S., Calvino, J. J., Cifredo, G. A., Gatica, J. M., Perez-Omil, J. A., Laachir, A., and Perrichon, V., *in* "Catalysis and Automotive Pollution Control, III" (A Frennet and J. M. Bastin, Eds.), Studies in Surface Science and Catalysis, Vol. 96, p. 419, Elsevier, Amsterdam, 1995.
7. Rogemond, E., Essayem, N., Fréty, R., Perrichon, V., Primet, M., Chevrier, M., Gauthier, C., and Mathis, F., *Catal. Today* **29**, 83 (1996).
8. Yao, H. C., and Yao, Y. F., *J. Catal.* **86**, 254 (1984).
9. Guénin, M., Breysse, M., Fréty, R., Tifouti, K., Marecot, P., and Barbier, J., *J. Catal.* **105**, 144 (1978).
10. Fréty, R., Da Silva, P. N., and Guénin, M., *Catal. Lett.* **3**, 9 (1989).
11. Fréty, R., Da Silva, P. N., and Guénin, M., *Appl. Catal.* **57**, 57 (1990).
12. Sanchez, M. G., and Gazquez, J. L., *J. Catal.* **104**, 120 (1987).
13. Harrison, B., Diwell, A. F., and Hallett, C., *Platinum Metals Rev.* **32**, 73 (1988).
14. Mitrofanova, A. N., Boronin, V. S., and Poltorak, O. M., *Zh. Fiz. Khim.* **46**, 32 (1972).
15. Rodríguez-Ramos, I., and Guerrero-Ruiz, A., *J. Catal.* **135**, 458 (1992).
16. Maatman, R. W., Mahaffy, P., Hoekstra, P., and Addink, C., *J. Catal.* **23**, 105 (1971).
17. Cusumano, J. A., Dembiski, G. W., and Sinfelt, J. H., *J. Catal.* **5**, 471 (1966).
18. O Cinneide, A. D., and Clarke, J. K. A., *Catal. Rev.* **7**, 213 (1972).
19. Mencier, B., Figueras, F., de Mourgues, L., and Trambouze, Y., *J. Chim. Phys.* **66**, 171 (1969).
20. Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).
21. Hertz, R. K., Gillespie, W. D., Petersen, E. E., and Somorjai, G. A., *J. Catal.* **67**, 371 (1981).
22. Fréty, R., Lévy, P. J., Perrichon, V., Pitchon, V., Primet, M., Rogemond, E., Essayem, N., Chevrier, M., Gauthier, C., and Mathis, F., *in* "Catalysis and Automotive Pollution Control, III" (A. Frennet and J. M. Bastin, Eds.), Studies in Surface Science and Catalysis, Vol. 96, p. 405, Elsevier, Amsterdam, 1995.
23. Yates, D. J., and Sinfelt, J. H., *J. Catal.* **8**, 348 (1967).
24. Bond, G. C., and Hui, L., *J. Catal.* **147**, 346 (1994).
25. Hoyos, L. J., Primet, M., and Praliaud, H., *J. Chem. Soc. Faraday Trans.* **88**, 113 (1992).
26. Primet, M., El Azhar, M., Fréty, R., and Guénin, M., *Appl. Catal.* **59**, 153 (1990).
27. Bernal, S., Calvino, J. J., Cifredo, G. A., Laachir, A., Perrichon, V., and Herrmann, J. M., *Langmuir* **10**, 717 (1994).
28. Bernal, S., Calvino, J. J., Cifredo, G. A., Rodríguez-Izquierdo, J. M., Perrichon, V., and Laachir, A., *J. Chem. Soc. Chem. Comm.* 460 (1992).
29. Bensalem, A., Bozon-Verduraz, F., and Perrichon, V., *J. Chem. Soc. Faraday Trans.* **91**, 2185 (1995).
30. Anderson, J. R., "Structure of Metallic Catalysts", Academic Press, London, 1975.
31. Rochefort, A., thesis, Paris, 1992.
32. Azhar, M. El, thesis, Lyon, 1989.