ELSEVIER

Catalysis Today 29 (1996) 83–87

CATALYSIS TODAY

Influence of the activation temperature on the metal accessibility in model three-way catalysts

E. Rogemond [a], N. Essayem [b], R. Fréty [a], V. Perrichon [a,*], M. Primet [a],
M. Chevrier [c], C. Gauthier [c], F. Mathis [c]

[a] *Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 9977 CNRS / UCB Lyon I, 43 bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*
[b] *Institut de Recherches sur la Catalyse, 2 avenue Einstein, 69626 Villeurbanne Cedex, France*
[c] *Régie Nationale des Usines Renault, 8-10 avenue Emile Zola, 92109 Boulogne Billancourt Cedex, France*

Abstract

The influence of the reduction temperature on the accessibility of the metallic surface was studied on model ceria–alumina supported platinum or rhodium catalysts. For a 0.5% Pt–Ce/Al solid, the H/M values, deduced from hydrogen irreversible chemisorption, decrease deeply with T_r, the reduction temperature, from 60% at $T_r = 300°C$ to 19% at $T_r = 500°C$. This can be attributed to strong interactions between ceria and platinum, since, the initial H_2 chemisorption could be restored after reoxidation. The presence of $BaSO_4$ in the support accelerates the loss of metallic area, because of sulfur poisoning of the platinum surface. For $T_r = 300°C$, the dispersion values were in agreement with those deduced from FTIR spectroscopy of adsorbed CO. In the case of rhodium, a 37% H/M dispersion was obtained, which did not change when T_r was increased from 300 to 500°C. For two industrial Pt–Rh three-way catalysts, the behaviour was found similar to that of platinum, the amount of chemisorbed hydrogen decreasing for $T_r > 350°C$. Thus, in the three-way catalysts characterization, the maximum metal accessibility is obtained after a reduction at 300°C.

Keywords: Pt catalysts; Rh catalysts

---

1. Introduction

One of the most frequently used method to measure the accessibility of a metallic surface is the irreversible hydrogen chemisorption performed at room temperature [1]. In the case of platinum metals, it is also possible to confirm this measure by a subsequent titration of the H_2 uptake by gaseous oxygen titration [2,3]. However, the accessibility of the metallic surface depends strongly on the activation conditions and also on the metal and support specific properties. Indeed, severe restrictions may limit the validity of the measurements:

1. The reduction temperature is too low, the precursor may not be fully reduced.
2. The reduction temperature is too high, a loss of active phase may occur due to metal sintering. It is also well established that high reduction temperatures of metals supported on easily reducible oxides (TiO_2, CeO_2) give rise to strong metal support interaction (SMSI) which modify the chemisorptive properties of the metal [4–7].

---

[*] Corresponding author.

SSDI 0920-5861(95)00272-3

3. Hydrogen spillover on the support is possible, resulting in a higher H_2 uptake.
4. When oxygen storage takes place on the support, the O_2 titration method is not valid.

Three-way catalysts are multicomponents systems which contain low loadings of precious metals deposited on alumina support modified by large amount of ceria. Other elements like Ba are often added to the washcoat. Ba is supposed to maintain the high surface area at elevated temperature [8]. 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. Since ceria is a reducible oxide and contributes to oxygen storage [9], it seems not possible to use gaseous oxygen titration to check the dispersion of the metals. In addition, H_2 spillover was found to occur very easily on ceria support at room temperature for a number of M/CeO_2 [10,11], which would invalidate the measurement of the accessible metallic area. However, in the case of Rh/CeO_2, it has been also observed that the hydrogen spillover rate decreases when the reduction temperature is increased from room temperature to 500°C [12]. At this temperature, no evidence of SMSI was obtained [12,13], although it could depend on the rhodium loading [14]. These observations suggest that it could be possible to optimize the activation conditions in order to suppress both the H_2 spillover on the support and the SMSI effect, but also to obtain a metallic phase fully reduced and not sintered.

In this work, related to the characterization of three-way catalysts, we have studied the influence of the reduction temperature on the accessibility of the metallic surface measured by irreversible hydrogen chemisorption (H/M). The model solids were two monometallic platinum or rhodium catalysts supported on either alumina or ceria–alumina. A support containing $BaSO_4$ was also prepared in order to investigate the effects of Ba and S additives in the washcoat. To validate the H/M value in the case of the optimized temperature, the metallic area was also measured by FTIR spectroscopy of adsorbed CO. Finally, we have investigated for comparison, the behaviour of two commercial three-way catalysts (Pt, Rh/Ce–Al/Cordierite).

2. Experimental

2.1. Catalysts preparation

The ceria–alumina support preparation has been already described. A toluene $Ce(acac)_3$ solution was put in contact with the hydroxyl groups of a SCM129 Rhône–Poulenc alumina support (107 m^2 g^{-1}). After drying under vacuum at 100°C, the solid was further calcined at 400°C [15]. The procedure was repeated two times to obtain the desired cerium content. The progressive disparition of the hydroxyl groups when the cerium content increased, as evidenced by the IR spectroscopy of adsorbed CO_2 and the high coverage of alumina by ceria for the resulting support were in favour of a nearly complete grafting of cerium acetyl acetonate entities on the alumina [15]. A ceria–alumina sample (21.9 wt.-% CeO_2) was also modified by adding 3.4 wt.-% $BaSO_4$ as follows. A suspension of $BaSO_4$ particles was added to a suspension containing the CeO_2–Al_2O_3 support. The resulting one was homogenized for 30 min at room temperature. After removal of water under reduced pressure at 80°C, the sample was calcined at 400°C in flowing air. This solid can be considered as an intimate deposit of $BaSO_4$ on the ceria–alumina support.

Table 1
Chemical analysis of the catalysts (wt.-%)

	Pt	Rh	Ba	Ce	S
0.5 Pt/Al	0.57				
0.5 Pt/Ce–Al	0.59			15.9	
0.5 Pt/Ce–Al + $BaSO_4$	0.56		1.92	17.6	0.46
0.5 Rh/Al		0.46			
0.5 Rh/Ce–Al		0.45		19.4	
COM1 [a]	0.49	0.10	2.14	20.5	0.49
COM2 [a]	0.68	0.07	2.00	19.0	0.39

[a] Calculated on a washcoat basis.

These supports were impregnated with aqueous solutions of H_2PtCl_6 or $RhCl_3$ in order to obtain five samples: 0.5 wt.-% Pt/Al, 0.5 wt.-% Rh/Al, 0.5 wt.-% Pt/Ce–Al, 0.5 wt.-% Rh/Ce–Al and a 0.5 wt.-% Pt/Ce–Al + Ba. After drying one night under vacuum at 110°C, they were treated for 2 h at 500°C under flowing nitrogen. The specific surface areas were comprised between 103 and 110 $m^2\ g^{-1}$. The chemical analysis data are given in Table 1, together with those of two commercial catalysts studied for comparison (5/1 and 10/1 PtRh) and referenced as COM1 and COM2. The variations in the cerium content originate from different support preparations. Our model catalysts are very representative of the industrial solids, except for the rhodium content which is five times lower for the later.

2.2. Hydrogen chemisorption measurements

They were performed in static at room temperature in a conventional glass volumetric set up. Before determining the H_2 chemisorption isotherms, the sample was evacuated 1 h at 450°C. After adjusting the reduction temperature (between 150 and 500°C), H_2 (20 Torr) was introduced in the cell for 1 h and then removed. This procedure was repeated once again to eliminate the water produced by the reduction and finally the reduction step was continued for one night. Then, the catalyst was evacuated for 2 h at the reduction temperature and cooled to room temperature before chemisorption.

The amounts of total and reversible hydrogen uptakes have been obtained by extrapolating the quasilinear portions (0–10 Torr) of the isotherm to zero pressure. The difference between the two previous values gave the amount of irreversible hydrogen uptake, from which the number of accessible metallic atoms was deduced, assuming a stoichiometry of 1 hydrogen atom per surface metal atom [1,2,16].

2.3. FTIR spectroscopy of adsorbed CO

Adsorption of carbon monoxide on platinum based catalysts gives rise to the formation of two CO bands, at ca. 2060 and 1830 cm^{-1}. It was established elsewhere [17] that the optical density of the first band, due to CO linearly bonded to platinum, was proportional to the metallic area. Thus, by using this method, it is possible to discriminate the adsorption on the metal from the adsorption on the support. For the FTIR study of the adsorption of CO, we followed the procedure previously described [17]. The catalysts were used as self-supported wafers and reduced according to the procedure described above for H_2 chemisorption.

3. Results and discussion

Table 2 gives the changes in the accessible metallic area H/M for reduction temperatures T_r comprised between 150 and 500°C. Their evolution is shown in Fig. 1.

Let us first consider the behaviour of the

Table 2

Accessible metallic area (H/M in %) as a function of the reduction temperature

Reduction T(°C)	150	250	300	350	400	450	500
0.5 Pt/Al			68				62
0.5 Pt/Ce–Al	2.6	63	59 (51) [a]	61		48	19
0.5 Pt/Ce–Al + $BaSO_4$		20–40	65 (59) [a]	56		9.2	
0.5 Rh/Al			33				30
0.5 Rh/Ce–Al			37		37		36
COM1			33				4.1
COM2		26		24		9	1.4

[a] Values in brackets were deduced from FTIR spectroscopy of adsorbed CO.

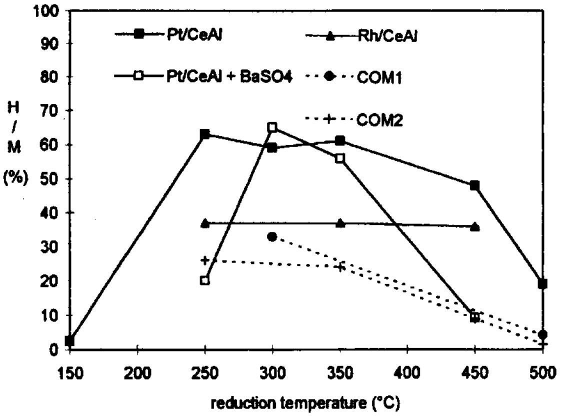

Fig. 1. Accessible metallic area (H/*M* in %) as a function of the reduction temperature.

platinum/ceria–alumina model catalyst. The amount of chemisorbed hydrogen is maximum and almost constant for T_r between 250 and 350°C, suggesting that, at lower temperatures, the reduction of platinum is not complete. The same behaviour was also observed for Pt/Al_2O_3 [18]. For T_r higher than 400°C, H/M decreases deeply, which is not the case for 0.5 Pt/Al_2O_3. Considering the low temperature, a sintering of the metallic particles can be ruled out. It can be rather supposed that the presence of ceria in the support induces a SMSI effect which decreases the accessibility of metal atoms. This phenomenon is well documented for Pt/CeO_2 and Pd/CeO_2 catalysts [7,8,19,20]. It will be shown below, that this loss in metal accessibility can be reversed after oxidation at 773 K, which is considered as an evidence of the SMSI.

The presence of $BaSO_4$ in the catalyst inhibits the reduction of platinum. At 250°C, two successive activations result in 20% and 40% dispersion. The maximum of 65% is obtained at 300°C. For higher temperatures the drop observed for 0.5 Pt/Ce–Al is amplified by the presence of $BaSO_4$. In addition to the SMSI, it can be explained by the poisoning of the platinum surface by hydrogen sulfide resulting from the sulfate ions reduction.

In the case of 0.5 Rh/Ce–Al, there is no change in the accessible metal area when T_r is increased from 300 to 500°C. That would indicate that no SMSI is obtained in these conditions with metallic rhodium, in agreement with previous observations on Rh/CeO_2 [12,13].

From these results, it appears that a temperature of 300°C could be a good compromise to reduce the catalysts before measuring the metal dispersion. However, to confirm this point, it is necessary to validate the values of dispersion by an other independent method. For that purpose, we have used FTIR of adsorbed CO for the two ceria–alumina platinum catalysts. The corresponding H/M values are reported also in Table 2. They are slightly smaller than those deduced from H_2 chemisorption. The IR technique being specific of the metallic surface, it is reasonable to ascribe the slight excess to some spillover of hydrogen from platinum on the reduced ceria surface. Nevertheless, the agreement between the two methods is fairly good (within 20%) and the values obtained from hydrogen can be considered as representative of the actual dispersion

The results for the two industrial catalysts are also given in Table 2. A behaviour similar to the platinum based catalysts is observed, indicating that SMSI effects due to the presence of platinum are effective and that the dispersions obtained after a reduction at 300°C are reliable. However, it can be remarked that the total dispersion is two times lower than our model catalysts, although the metallic content is lower. The difference could originate from the preparation method.

To prove that the reduction at high temperature (500°C) creates the SMSI effect and does not change the size of the particles, we have studied the reversibility of the surface state by performing a reoxidation at 500°C (in order to destroy the interaction) followed by a new reduction at 300°C. Table 3 gives the changes in the hydrogen chemisorption after the successive treatments.

The hydrogen chemisorption capacities are almost completely recovered for all the catalysts indicating the reversibility of the phenomenon,

Table 3
H/M (%) dispersion. Reversibility of SMSI effect by oxidation of platinum based catalysts

Catalyst	T_r = 300°C	T_r = 500°C	T_r = 300°C after reoxidation at 500°C
0.5 Pt/Ce–Al	63	19	55
0.5 Pt/Ce–Al + Ba	65	9.2	65
COM1	33	4.1	41
COM2	26	1.4	30

in agreement with literature [5–8,19,20]. For the model catalyst modified by $BaSO_4$, it is also clear that the oxidative treatment has fully eliminated adsorbed sulfur atoms from the platinum; they are oxidized into SO_3 which are trapped by the support. Concerning the industrial catalysts, the metal accessibility is even higher after the HT oxidation–LT reduction cycle. Among numerous hypothesis, this could be assigned to a re-dispersion of platinum or rhodium after the oxidation at 500°C [21]. Changes in the spillover extent due to the elimination of chlorine can be also considered [22].

4. Conclusion

If the dispersion of precious metals in the three-way catalysts is often measured after reduction at 300°C, no explanations have been given to justify the choice of this temperature. In the present study, it is shown that hydrogen chemisorption can become a reliable method for metal dispersion measurement provided that an appropriate prereduction temperature (300°C) is chosen. It is sufficient to reduce the precious metals without reducing the sulfate compounds and induces no or very limited SMSI effects.

References

[1] J.J.F. Scholten, A.P. Pijpers and A.M.L. Hustings, Catal. Rev. Sci. Eng., 27 (1985) 151.
[2] J.E. Benson and M. Boudart, J. Catal., 4 (1965) 705.
[3] D.J. Suh, T.J. Park and S.K. Ihm, J. Catal., 149 (1994) 486.
[4] B. Harrison, A.F. Diwell and C. Hallett, Platinum Metals Rev., 32 (1988) 73.
[5] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc., 100 (1978) 170.
[6] J.P. Belzunegui, J. Sanz and J.M. Rojo, J. Am. Chem. Soc., 114 (1992) 6749.
[7] M.G. Sanchez and J.L. Gazquez, J. Catal., 104 (1987) 120.
[8] D. Kalakkad, A.K. Datye and H. Robota, Appl. Catal. B Environ., 1 (1992) 191.
[9] H.C. Yao and Y.F. Yao, J. Catal., 86 (1984) 254.
[10] J.T. Miller, B.L. Meyers, F.S. Modica, G.S. Lane, M. Vaarkamp and D.C. Koningsberger, J. Catal., 143 (1993) 395.
[11] S. Bernal, J.J. Calvino, G.A. Cifredo, J.M. Rodriguez-Izquierdo, V. Perrichon and A. Laachir, J. Catal., 137 (1992) 1.
[12] S. Bernal, J.J. Calvino, G.A. Cifredo, A. Laachir, V. Perrichon and J.M. Herrmann, Langmuir, 10 (1994) 717.
[13] S. Bernal, F.J. Botana, J.J. Calvino, M.A. Cauqui, G.A. Cifredo, A. Jobacho, J.M. Pintado and J.M. Rodriguez-Izquierdo, J. Phys. Chem., 97 (1993) 4118.
[14] A. Trovarelli, G. Dolcetti, C. de Leitenburg, J. Kaspar, P. Finetti and A. Santoni, J. Chem. Soc., Faraday Trans., 88 (1992) 1311.
[15] R. Fréty, P.J. Lévy, V. Perrichon, V. Pitchon, M. Primet, E. Rogemond, N. Essayem, M. Chevrier, C. Gauthier and F. Mathis, Stud. Surf. Sci. Catal., 96 (1995) 405.
[16] G.C. Bond and L. Hui, J. Catal., 147 (1994) 346.
[17] M. Primet, M. El Azhar, R. Fréty and M. Guenin, Appl. Catal., 59 (1990) 153.
[18] D. Rajeshewer, A.G. Basrur, D.T. Gokak and K.R. Krishnanurthy, J. Catal., 150 (1994) 135.
[19] C. Binet, A. Jadi, J.C. Lavalley and M. Boutonnet-Kizling, J. Chem. Soc., Faraday Trans., 88 (1992) 2079.
[20] L. Fan and K. Fujimoto, J. Catal., 150 (1994) 217.
[21] J.Z. Shyu and K. Otto, Appl. Surf. Science, 32 (1988) 246.
[22] S. Bernal, J.J. Calvino, G.A. Cifredo, J.M. Gatica, J.A. Perez-Omil, A. Laachir and V. Perrichon, Stud. Surf. Sci. Catal., 96 (1995) 419.