Application of electroless procedures to the preparation of palladium catalysts

A. Bensalem, G. Shafeev [1] and F. Bozon-Verduraz [2]

Laboratoire de Chimie des Matériaux Divisés et Catalyse, Université Paris 7, 2, place Jussieu, 75250 Paris Cedex 05, France

Received 30 November 1992; accepted 8 December 1992

The influence of various (laser, UV lamp and thermal) activation treatments on the diffuse reflectance and ESR spectra of CeO_2 are examined. Ceria-supported palladium catalysts are prepared by electroless deposition of the metal from palladium chloride and hydrazine hydrate solutions. The atomic defects induced in ceria by the activation procedures appear to initiate the palladium deposition.

Keywords: Palladium–ceria catalysts; electroless; photoactivation; diffuse reflectance

1. Introduction

The photoassisted deposition of noble metals from their salts or complexes is a well known process which has recently been applied to the preparation of monometallic and bimetallic catalysts [1,2]. In this process, a semiconducting carrier is irradiated with photons of energy greater than the band gap in the presence of the metal precursor in solution. The reduction of the noble metal cation is achieved by the electrons produced under illumination provided that the associated holes are rapidly consumed by the reaction medium [1,2].

On the other hand, *electroless plating* is an ancient procedure [3] which has recently received renewed attention, particularly in the field of microelectronics [4]. To the best of our knowledge, it has not been used in the preparation of supported metal catalysts. Electroless deposition is a mixed potential reaction consisting of the anodic oxidation of a reducing agent and the cathodic reduction of the metal precursor. The electrons are transferred from the reducing agent to the metal ion *via the surface sites* of a solid substrate. When using a dielectric substrate, a catalytic procedure is believed to be necessary for electroless deposition [4] and the catalytic sites may be *atomic defects* created by irradiation [5]. With *insulating carriers*

[1] On leave from the General Physics Institute of the Russian Academy of Sciences.
[2] To whom correspondence should be addressed.

(e.g. alumina), which are transparent in the UV–visible region, irradiation with UV light generates defects only if air breakdown and plasma formation take place near the surface of the samples [5]. With *semiconducting carriers*, high energy density radiations create atomic defects which may remain after illumination, as opposed to the photoproduced hole–electron pairs involved in the process described above.

Our objective is to prepare supported metal catalysts through irradiation of a semiconducting carrier to induce the electroless deposition of the metal precursor. This paper is devoted to the preparation of palladium catalysts supported on ceria which is a wide band gap semiconductor (3.1 ev) [6].

2. Experimental

2.1. MATERIALS

The CeO_2 samples (Rhône-Poulenc) were used either as a powder (specific surface area 115 m^2/g) or as sintered and annealed pellets. $PdCl_2$ (Engelhard, France) was the metal source and hydrazine hydrate the reducing agent.

2.2. TECHNIQUES

The photoactivation of CeO_2 was performed with UV laser beam. Two laser sources were used: either N_2 laser ($\lambda = 337$ nm, 3 mJ/pulse) or XeCl excimer laser ($\lambda = 308$ nm, 60 mJ/pulse, pulse duration = 30 ns). To provide the necessary level of energy density on the sample surface, the laser radiation was focussed with a 10 cm focal length quartz lens. A mercury UV lamp was also occasionally used. Irradiation was carried out either in open air or in vacuo through a quartz tube.

Thermal activation procedures were carried out for comparison. The *unreduced samples* were obtained by pretreatment in a flux of oxygen (18 ℓ/h) during 15 h at 673 K, and evacuation for 15 min at ambient temperature. In some cases, the outgassing temperature was fixed at 1073 K for 15 h. The *reduced samples* were submitted to an additional heating in an hydrogen flow (18 ℓ/h) at $T_r = 573$–773 K for 2 h before evacuation at 10^{-4} Torr.

Electron spin resonance (ESR) spectra of the samples were recorded at 77 K on a Bruker ER 200D spectrometer operating at 9.2 MHz. The diffuse reflectance spectra (DRS) of both CeO_2 powder and pellets were recorded in the 230–700 nm range with a Beckmann 5270 UV–visible spectrometer connected to a microcomputer and equipped with an integrating sphere coated with $BaSO_4$.

The metallization of CeO_2 samples was performed with a Pd electroless plating solution prepared as follows. Addition of an excess of concentrated ammonia to a $PdCl_2$ solution under agitation gave a clear solution of palladium tetrammine complex, as checked by UV–visible spectroscopy. After adding a stabilizer like EDTA

[7], cerium dioxide was immersed in the solution maintained at a fixed temperature between 290 and 310 K and the resulting suspension was stirred while pouring hydrazine hydrate. Emission of nitrogen bubbles was then detected (see below). After 5 min contact, the solid phase was filtered and dried at 343 K in air for 15 h.

Typical quantities are:

[Pd]: 2.25×10^{-2} mol ℓ^{-1}, [EDTA]: 7×10^{-3} mol ℓ^{-1}, $T = 303$ K

[N_2H_4, H_2O]: 4×10^{-2} mol ℓ^{-1}, CeO_2: 10 g per 200 ml of solution.

The redox reaction may be written as follows

$$2Pd(NH_3)_4^{2+} + N_2H_4 + 4OH^- \xrightarrow{(CeO_2)} 2Pd^0 + 8NH_3 + N_2 + 4H_2O\,.$$

Preliminary experiments showed that, *in the above conditions*, no palladium deposit occurs *in the absence of cerium dioxide*.

The elemental analysis of the metallized samples was determined with inductively coupled plasma emission spectroscopy. The average particle size of the Pd deposit was calculated according to the Scherrer formula from the halfwidth of the (hkl) X-ray diffraction lines corrected for instrumental broadening (Cu Kα radiation on a Siemens D 500 diffractometer).

3. Results and discussion

3.1. ACTIVATION OF CERIUM DIOXIDE

3.1.1. Diffuse reflectance studies

Fig. 1 compares the diffuse reflectance spectra of samples obtained by various activation methods: irradiation in air by a XeCl laser beam or by a mercury UV-lamp, heating in vacuo at 1073 K for 15 h. In the case of the laser-irradiated sample, the induced absorption disappears within a few seconds if the energy density is lower than 1 J/cm^2, in contrast with the results previously obtained on alumina [5]. When the energy flux amounts to 2 J/cm^2, the induced absorption decays slowly with time at room temperature in air and disappears after several days. The spectrum recorded immediately after irradiation by 500 pulses at 2 Hz shows a broad band with a maximum near 440 nm ($\approx$ 23000 cm^{-1}) while irradiation with the mercury lamp for 6 h induces a weaker absorption band in the same range. In the case of a sample heated in vacuo at 1073 K, the band maximum is located near 650 nm (16000 cm^{-1}), as previously reported for CeO_2 prereduced by hydrogen at $T \geqslant 573$ K [8] or outgassed at 1073 K [9].

3.1.2. ESR studies

When a CeO_2 sample *not reduced by hydrogen* is irradiated in vacuo with the N_2 laser beam, it shows an anisotropic ESR signal (A) with $g_{\parallel} = 2.033$ and $g_{\perp} = 2.014$ aside with a very weak isotropic signal (B) ($g = 1.965$) (fig. 2).

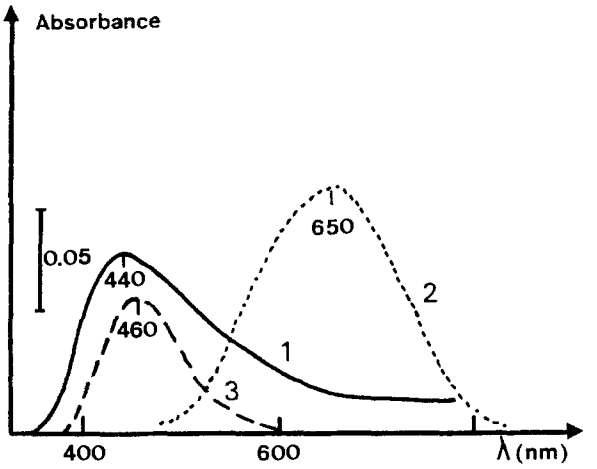

Fig. 1. Diffuse reflectance spectra (recorded at 293 K) of CeO_2 samples submitted to various treatments: (1) irradiation in air with XeCl laser beam (2 J/cm^2, spectrum recorded 30 min after irradiation; (2) heating in vacuo at 1073 K for 15 h; (3) irradiation in air with an UV mercury lamp for 6 h, spectrum recorded 30 min after irradiation. All spectra were recorded with untreated ceria as a reference.

Other samples were reduced by H_2 before ESR examination *without any irradiation*. For $T_r = 573$ K, no signal is detected. On the other hand, when the reduction temperature is increased to 773 K, the spectrum does show only an isotropic signal (B) with a calculated g-factor equal to 1.965 (fig. 2).

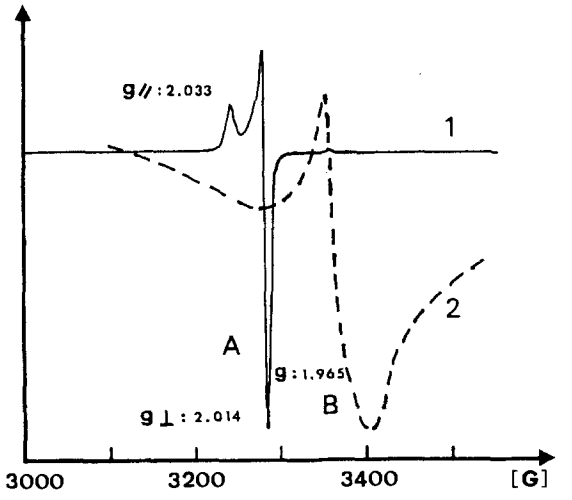

Fig. 2. ESR spectrum (X band) recorded at 77 K of CeO_2 samples: (1) unreduced and photoactivated with N_2 laser; (2) prereduced by H_2 at 773 K for 2 h without irradiation.

3.1.3. Discussion

The surface of non-stoichiometric CeO_2 contains paramagnetic species with an isotropic value $g = 1.965$. These species were observed previously in CeO_2 heated in vacuum at 773 K and this signal was attributed either to Ce^{3+} ions [10] or to quasi-free electrons in a CeO_2 matrix [11]. A similar isotropic signal (B) is detected in a CeO_2 sample irradiated with N_2 laser in vacuo (fig. 2). It is pertinent to note, however, that Ce^{3+} ions cannot be detected with ESR methods because of their very short relaxation time in CeO_2 matrix [11], though the presence of these ions in partially reduced CeO_2 was proved with other techniques [8]. In addition, the laser-irradiated samples show a strong anisotropic signal (A) with $g_\perp = 2.033$ and $g_\parallel = 2.014$ (fig. 2), which has not been observed in oxygenless environment. This anisotropic signal was attributed to the molecular ion O_2^- adsorbed on Ce^{4+} lattice ions [12]. The formation of this species requires a significant amount of oxygen. In our conditions, the oxygen may originate from at least two sources: (i) the oxygen of the residual gas atmosphere in the irradiation cell, (ii) the oxygen released from the CeO_2 lattice during laser irradiation. The latter source seems to be more probable, since the residual pressure was only 10^{-4} Torr. Summing up, one may conclude that laser irradiation of CeO_2 at flux above 1 J/cm^2 results in the formation of non-stoichiometric samples with oxygen vacancies and Ce^{3+} ions. It is also relevant to note that, unlike the absorption band produced by laser irradiation in Al_2O_3 [5], the band observed in laser-irradiated ceria disappears with time even at room temperature. Besides, the defects in CeO_2 may be generated by heating in H_2 at moderate temperature or in vacuo at high temperature, while the creation of defects in Al_2O_3 requires the air breakdown (plasma) on the Al_2O_3 surface during the laser irradiation. The difference between Al_2O_3 and CeO_2 arises obviously from the value of the band gap width (about 9 and 3.1 eV, respectively). The energy of formation of oxygen vacancies is related to these values. As their energy level is closer to the bottom of the conduction band, the defects in CeO_2 may recombine faster than in Al_2O_3 at ambient temperature. However, the maxima of absorption of CeO_2 irradiated with laser and UV lamp in air (fig. 1, curves 1 and 3) are shifted to shorter wavelengths compared to the absorption band induced by heating CeO_2 in vacuo (fig. 1, curve 2) or in H_2 (maximum absorption at 650 nm). The former may correspond to "non-equilibrium" defects produced by fast heating of CeO_2 at normal partial pressure of O_2, while the latter is obtained at *low* partial pressure. According to both reflectance spectra and ESR data, the defects could be color centers such as oxygen vacancies with trapped electrons and Ce^{3+} ions.

3.2. PALLADIUM DEPOSITION

The pellet samples irradiated with XeCl laser beam at energy flux higher than 1 J cm^{-2} show an activity towards Pd reduction from the electroless solution. Namely, the irradiated areas of the CeO_2 pellet are covered with metallic Pd after dipping into the Pd electroless bath and the metal deposit is restricted to the laser-

irradiated areas. In addition, there is a strong correlation between the radiation-induced absorption of CeO_2 and its activity towards metal deposition: the annealing of the irradiated CeO_2 pellet in air at 300°C for 2 h completely restores the diffuse reflectance spectrum of the initial sample. Simultaneously, the pellet is no more active for Pd deposition.

The Pd electroless solution was also used for the metallization of CeO_2 *powder* though the irradiation conditions of the powder are difficult to standardize. The powder sample (specific surface area: 115 m^2/g) was irradiated in open air during 10 min with a XeCl excimer laser beam (2 J/cm^2, 120 mJ/pulse, 10 Hz repetition rate) and was stirred during exposure. Irradiation also leads to the change of the absorption spectrum in the visible region as observed with pellets (fig. 1). The average size of the Pd particles in this sample was estimated to around 39 nm and the palladium content amounted to 8.94%. It is necessary to note, however, that almost any dielectric powder with a large specific area may provoke the metal deposition from electroless solutions because the electroless reduction of metals is essentially heterogeneous. In this way, a non-irradiated CeO_2 powder was also metallized, though the reaction rate in this instance was lower than for the irradiated powder. If the reaction proceeded up to the exhaust of the reducing agent (that is until the end of nitrogen bubbles emission), the Pd content was found to be nearly the same at otherwise equal conditions. However, the average grain size of Pd in the non-irradiated sample of CeO_2 powder was much larger (around 64 nm). In addition, if the powder sample was calcined at 1073 K in air, its surface area was sharply decreased (5 m^2/g) and no palladium deposition was noticed. Hence the defects appear to act as catalytic sites for electroless deposition. It is also relevant to report that no deposit was detected either on a high surface area silica (380 m^2/g) when using the same electroless solution as above *at the same temperature*. Hence it appears that the CeO_2 powder contains enough defects to induce the palladium deposition without preliminary irradiation. Investigations are in course now to get more information about the nature of these defects. Finally, if the temperature is greater then about 360 K, reduction of palladium ions occurs in the bulk of the solution.

Summing up, electroless deposition is a mixed potential reaction: both the oxidation of the reducing agent and the reduction of the metal ion take place at the same surface site whose electrochemical potential fits the redox process. From this point of view, the electroless deposition of Pd can be promoted only if the energy level of the defect fits the redox potential of Pd reduction and hydrazine hydrate oxidation. In other words, electrons are transferred from the reducing agent to the metal ion in the vicinity of the surface defect. Irradiation of the powder increases the number of defects and this results in decreasing the Pd particle size since the same quantity of Pd is shared between a larger number of defects.

4. Conclusion

UV-irradiation of CeO_2 with laser beam or conventional source leads to the formation of surface defects (oxygen vacancies and Ce^{3+} ions). These defects, which are characterized by ESR signals and absorption in the visible range, promote the Pd deposition from electroless plating solutions. In addition, non-irradiated CeO_2 samples presenting a large surface area may also induce metal deposition but with a smaller reaction rate. The influence of the nature of the palladium precursor and of the reaction medium, as well as the role of the temperature and of the activation conditions (photo or thermal activation) are now under investigation to achieve a better control of the Pd particle size.

Acknowledgement

Mrs. Lalo, from the Laboratoire de Chimie des Surfaces, and Mr. Ranson from the Department des Recherches Physiques (Université Paris 6), are gratefully acknowledged for laser facilities. Thanks are also due to the Laboratoire de Réactivité de Surface et Structure (Université Paris 6) for ESR and X-ray diffraction measurements.

References

[1] H. Yoneyama, N. Nishimura and H. Tamura, J. Phys. Chem. 85 (1991) 268.
[2] A. Fernandez, G. Munuera, A.R. Gonzalez- Elipe, J.P. Espinos, J.M. Herrmann, P. Pichat and C. Leclercq, Appl. Catal. 57 (1990) 191.
[3] W.A. McRae, in: *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd Ed., Vol. 8 (1979) p. 738.
[4] M. Paunovic and J. Ohno, eds., *Proc. Symp. Electroless Deposition of Metals and Alloys* (The Electrochemical Society, Pennington, 1988).
[5] G. Shafeev, *Proc. of EMRS*, Spring Meeting, paper B VI, 3, Strasbourg 1992, in press.
[6] C.A. Hogard and Z.T. Al Dhhan, Phys. Rev. B137 (1986) K157.
[7] R.N. Rhoda, Trans. Inst. Metal Finishing 39 (1958) 82; J. Electrochem. Soc. 108 (1961) 707.
[8] A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J.C. Lavalley, J. El Fallah, L. Hilaire, F. Le Normand, E. Quéméré, G. Noël Sauvion and O. Touret, J. Chem. Soc. Faraday Trans. 87 (1991) 1601.
[9] A. Rakaï, A. Bensalem, J.C. Muller, D. Tessier and F. Bozon-Verduraz, 10th Int. Congr. on Catalysis, Budapest 1992 (Elsevier, Amsterdam), in press.
[10] M. Che, J.F.J. Kibblewhite, A.J. Tench, M. Dufaux and C. Naccache, J. Chem. Soc. Faraday Trans. I 69 (1973) 857.
[11] M. Steinberg, Israel J. Chem. 8 (1970) 877.
[12] M. Che and A.J. Tench, Adv. Catal. 32 (1983) 1.