JOURNAL OF CATALYSIS **159,** 361–367 (1996)
ARTICLE NO. 0098

An *in Situ* Electrical Conductivity Study of a CeO_2 Aerogel Supported Palladium Catalyst in Correlation with the Total Oxidation of Propane

Jean-Marie Herrmann,[1] Can Hoang-Van, Lucie Dibansa, and Rondronirina Harivololona

URA au CNRS "Photocatalyse, Catalyse et Environnement," Ecole Centrale de Lyon, B.P. 163, 69131 Ecully Cédex, France

Received March 13, 1995; revised June 7, 1995; accepted October 13, 1995

The electrical conductivity of a Pd/CeO_2 aerogel catalyst has been measured *in situ* during the reduction of the catalyst in H_2 and during the oxidation of propane, both carried out during programmed heating. The results can be rationalized on the basis of (i) the formation of anionic vacancies in ceria upon reduction, (ii) the subsequent electron transfer from reduced ceria to Pd, a transfer which persists during the catalytic reaction, (iii) the partial reoxidation of the surface of ceria in the presence of the reaction mixture at temperatures <523 K, and (iv) the reduction of CeO_2 at the Pd–CeO_2 interface by H atoms abstracted from propane chemisorbed on Pd at temperatures >523 K, this abstraction being thereby favored by the support. Attempts have been made to correlate the various conduction activation energies with corresponding surface reactions.

INTRODUCTION

In recent years, cerium dioxide has been increasingly used as a promoter for automotive gas conversion (1). Current three-way catalysts to treat automotive exhaust consist of two transition metals (Pt or Pd, Rh) deposited on alumina containing up to ca. 25 wt% CeO_2. Investigations on the role of ceria have pointed out its ability to release or store oxygen when necessary (2). Therefore, ceria is expected to be in a more or less reduced state on these catalysts, which points out that a detailed knowledge of the oxidation state of cerium under the reaction mixture is needed.

In a previous study of the semiconductivity of the Ni/CeO_2 system in relation with its methanation activity (3), one of us has shown that the observed catalytic behavior could be interpreted in terms of an electron enrichment of the nickel particles and by assuming the presence of active sites at the metal-support interface made up of surface nickel atoms and oxygen vacancies.

The aim of the present work was to investigate the electronic state of a Pd/CeO_2 aerogel catalyst by measuring *in situ* its electrical conductivity during its reduction by H_2 and then in the presence of the test reaction mixture ($C_3H_8 + 5O_2$). An attempt was made to correlate these measurements with the catalytic activity of the solids in the total oxidation of propane. CeO_2 aerogel was used as a carrier because oxide aerogels have been shown to be efficient supports for Pd catalysts in the oxidation of propane (4) and in the CO + NO + O_2 reaction (5).

EXPERIMENTAL

Materials

The ceria aerogel support was prepared by the sol–gel process combined with the supercritical drying technique as previously described (6). It can be briefly recalled that the CeO_2 aerogel was obtained by hydrolyzing cerium IV acetylacetonate, dissolved in methanol, with a stoichiometric amount of added water and by drying the alcogel in an autoclave above the critical temperature and pressure of methanol. The resulting ceria aerogel was amorphous and had a surface area of $104\ m^2 \cdot g^{-1}$.

A 1 wt% Pd/CeO_2 aerogel catalyst was prepared by impregnating the CeO_2 aerogel with a solution of $Pd(acac)_2$. Before the test of propane oxidation, the solid was reduced *in situ* in a hydrogen flow ($50\ cm^3$/min) at 773 K for 3 h (heating rate: $8\ K \cdot min^{-1}$). The reduced catalyst had a surface area of $32\ m^2 \cdot g^{-1}$ and exhibited the cubic phase of crystalline CeO_2. The fraction of accessible metallic surface, as determined by infrared spectroscopy of CO chemisorbed on Pd following the method reported by Duplan and Praliaud (7), was 4%. This low value of CO uptake in comparison with usual supported Pd catalysts suggests the establishment of the SMSI state (8) in the reduced catalyst.

Activity Measurements

The activity in propane oxidation was measured in a flow system at increasing temperature (heating rate: 1.4 $K \cdot min^{-1}$) in the range 423–773 K. Reactant and product gases were analyzed by gas chromatography with a thermal

---

[1] To whom correspondence should be addressed.

0021-9517/96 $18.00

conductivity detector (CO_2) and a flame ionization detector (C_3H_8). The catalyst sample (50 mg) was mixed with inactive α-Al_2O_3 (150 mg). The pretreatment of both Pd/CeO_2 and CeO_2 with the alumina diluent added consisted in an *in situ* reduction at 773 K (*vide supra*). The reaction mixture was composed of 0.3% C_3H_8 and 1.5% O_2 in N_2 (stoichiometric mixture) and the total flow rate was 20 dm^3/h, which gave a GHSV of ca. 80,000. CO_2 and H_2O were the only two products detected.

Electrical Conductivity Measurements

Conductivity cell. The semiconductivity of the different samples, has been investigated by using a cell specially designed to study the electronic interactions between powdered samples and various gaseous atmospheres (9). This cell has previously been employed for studying pure, doped, mixed oxides, sulfides and metal/semiconductor catalysts.

About 390 mg of catalyst were placed between two platinum electrodes under a constant pressure of ca. 10^5 Pa which is compatible with good interparticle electrical contacts and with a good gas–solid interaction over the whole surface of the solid. The temperature of each electrode was given by a thermocouple whose wires were also used as connections for electrical measurements. The electrical resistance of the samples was measured with various *R*-meters according to the range investigated: a Kontron multimeter (model DMM 4021) for resistances lower than $2 \times 10^6\ \Omega$ (dc voltage = 1 V) or with a digital teraohmmeter (Guildline Instruments, (model 9520)) for higher values (dc voltage from 1 to 10 V). It was previously shown that powdered semiconducting oxides behave as bulk conductors (9) and the electrical conductivity of the powdered samples can be formally written as

$$\sigma = 1/\rho = 1/R \times t/S, \qquad [1]$$

where ρ is the resistivity, R is the electrical resistance, and (t/S) is the geometric factor (t is thickness, generally chosen between 0.4 and 0.5 cm, and S the section area of the electrodes (diameter 1.00 cm)). Conductivity measurements carried out on powders provide intrinsic bulk values for the material, when surface and bulk conductivities are similar. In that case, the experiments are identical to those carried out on single crystals, for which σ is equal to

$$\sigma = nq\mu, \qquad [2]$$

where n and μ are, respectively, the concentration and the mobility of the main charge carriers, and q is the elementary charge of the electron. For a powdered sample, the conductivity σ can be written as

$$\sigma = An, \qquad [3]$$

where A is a coefficient of proportionality which remains constant during the experiment and includes, besides q and μ, textural parameters, such as the number of interparticle contact points. Since, in this work, all the samples have BET surface areas of the same order of magnitude, coefficient A can be considered as nearly constant, whatever the solid. Hence, semiquantitative comparisons between solids may be made and electrical conductivity measurements provide an estimate of the variations in the concentration of the main charge carriers as a function of physical parameters such as temperature, oxygen pressure, nature, and pressure of gases, under conditions as close as possible to those of the catalytic reaction. Upon exposure to a gas atmosphere, it is likely that conduction effects at the surfaces dominate, as seems to be the case for the present results and was considered to be true for oxide catalysts (10–12). It is important to stress that values of σ are relative and not absolute.

Procedure. To perform the σ measurements under conditions as close as possible to those of the catalyst pretreatment and of the catalytic activity measurements, the following procedure has been observed:

— Outgassing of naked and of Pd $(acac)_2$-impregnated ceria at room temperature and subsequent introduction of 400 Torr of hydrogen (1 Torr = 133.3 Pa).

— Temperature programmed reduction (TPR) of the solid from room temperature to 773 K at a constant rate of 8 K/min. The temperature was maintained at 773 K for 3 h.

— Cooling from 773 to 423 K.

— Outgassing of H_2 and introduction of a stoichiometric reacting mixture ($1C_3H_8 + 5O_2$) under a total pressure of 13.7 Torr corresponding to that used in catalytic tests.

— *In situ* catalytic test carried out at a heating rate identical to that used in the dynamic flow reactor (1.4 K/min).

The conductivity measured is essentially that of the support (3, 9, 13, 14), since the metal loading of the catalyst is much lower than that corresponding to the percolation threshold (15). Therefore, the specific effect of the metal upon the electrical conductivity of the catalyst was evaluated from the differential analysis of the results obtained on Pd/CeO_2 and on bare CeO_2.

RESULTS AND DISCUSSION

1. Catalytic Test of Propane Oxidation

The light-off curves of Pd/CeO_2 and CeO_2 corresponding to the temperature programmed oxidation (TPO) of propane are shown in Fig. 1. The starting temperature for propane oxidation over Pd/CeO_2 was ca. 523 K, whereas that observed over bare CeO_2 was higher by about 150 K (ca. 673 K). At 773 K, 67 and 11% conversion levels were obtained for Pd/CeO_2 and CeO_2, respectively (Fig. 1). Therefore, CeO_2 aerogel exhibited some activity in propane oxidation in the temperature range examined, in contrast to Al_2O_3 aerogel which was completely inactive at 773 K, under identical conditions. Despite the low dispersion of

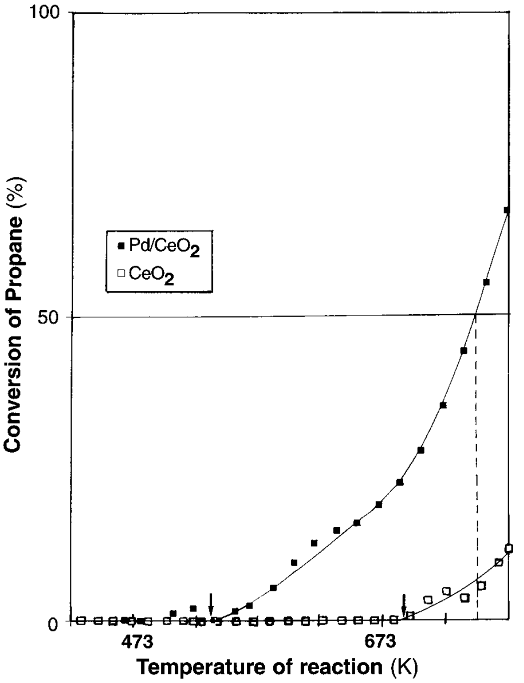

FIG. 1. Conversion of total oxidation of propane as a function of the reaction temperature (heating rate: 1.4 K/min) under stoichiometric mixture.

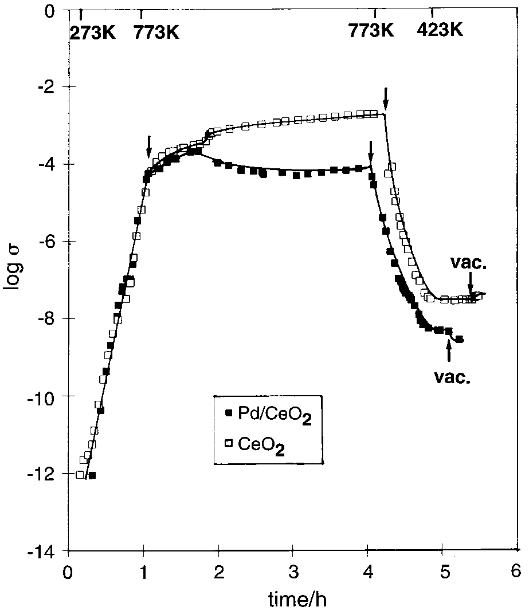

FIG. 2. Semilog plot of the kinetics of variation of the electrical conductivity σ (in Ω^{-1} cm^{-1}) of Pd/CeO_2 and CeO_2 during (i) TPR from 293 to 773 K in H_2 (400 Torr) (heating rate: 8 K/min), (ii) treatment at 773 K under 400 Torr H_2 for 3 h, and (iii) cooling in H_2 from 773 to 423K followed by outgassing(vac.) at 423 K.

Pd (4%), Pd/CeO_2 is much more active than CeO_2. It may be possible that the reacting mixture liberates some Pd particles during the reaction.

2. *In Situ* Electrical Conductivity Study of the Reduction of CeO_2 and Pd/CeO_2

2.1. *Temperature Programmed Reduction (TPR)*

The kinetics of the reduction by hydrogen is presented in the semilog plot $\log \sigma = f(t)$ of Fig. 2. At room temperature, both naked and impregnated ceria behave as an insulator. Upon heating, its conductivity increases by about 10 orders of magnitude. The linear variations of log σ versus time indicate an exponential variation of σ with time, i.e., with temperature because of the constant heating rate. This behavior indicates that during reduction ceria becomes a semiconductor whose conductivity follows the Arrhenius law,

$$\sigma = \sigma_o \exp(-E_c/RT), \qquad [4]$$

where E_c is the activation energy of conduction.

In agreement with previous studies concerning titania (13, 14) and ceria (3, 16), the high increase of σ is ascribed to the formation of anionic vacancies according to the reaction

$$O^{2-}_{(\text{lattice})} + H_2 \rightleftarrows H_2O(g) + V_o. \qquad [5]$$

The symbol V_o represents an anionic vacancy with two electrons trapped. It is a neutral entity with respect to the surface lattice of ceria. It can easily lose an electron by spontaneous ionization and becomes singly positively charged with respect to the solid:

$$V_o \rightleftarrows V_o^+ + e^-. \qquad [6]$$

Considering that in an *n*-type semiconductor such as ceria, the electrical conductivity is proportional to the main charge carrier concentration, *n* in Eq. [3] can be replaced by $[e^-]$:

$$\sigma = A[e^-]. \qquad [7]$$

According to Eqs. [5]–[7], the variation rate of σ gives access to the rate of reduction r_{red} of ceria by H_2:

$$r_{\text{red}} = -d[O^{2-}]/dt = +d[V^o]/dt = d[e^-]/dt = (1/A)d\sigma/dt. \qquad [8]$$

The identity of the curves $\log \sigma = f(t)$ for Pd/CeO_2 an CeO_2 submitted to the temperature programmed reduction indicates that both solids are reduced at the same rate and with the same activation energy of 268 kJ/mol. No catalytic effect of palladium on the rate of reduction of ceria was detected. This observation could appear somehow surprising, since it was previously shown that H_2 dissociation by the metal and subsequent transfer of H atoms to the support enhanced the reducibility of CeO_2 (17, 18). However, in the present case, there exist some special conditions: (i) $Pd(acac)_2$ is only partially reduced during TPR up to 773 K, because of the high heating rate employed (8 K/min) and

(ii) the Pd content is low (1 wt%) and a large fraction of this metal is present in the bulk as indicated by the low metal dispersion (4%). These conjugated factors can explain why a possible catalytic effect of Pd upon the surface reduction of ceria could not be detected under the present conditions by electrical conductivity variations.

2.2. Reduction at 773 K for 3 h

After about 2 h at 773 K in a hydrogen atmosphere, σ (CeO_2) continued to increase slightly, whereas σ (Pd/CeO_2) decreased slightly. The resulting difference in conductivity between the two solids was about one and a half order of magnitude after 3 h. This can be tentatively attributed to an electron transfer from CeO_2 to Pd according to

$$e^-(CeO_2) + (Pd) \rightleftarrows e^-_{Pd}. \qquad [9]$$

This electron transfer is thermodynamically due to the alignment of the Fermi levels of reduced ceria and of supported palladium. Actually, the Fermi level of a reduced oxide is increased by the high concentration of anionic vacancies and the high concentration of their corresponding ionized electrons (Eq. 6). This electron transfer from the support to the metal has been observed for other systems such as Pt/TiO_2 (13, 19, 20), Rh, Ni/TiO_2 (14), and Ni/CeO_2 (3), and has been considered as responsible, at least partially, for the origin of the SMSI state.

No values of the work function of ceria could be found in the literature since, because of the complexity of the electrical properties of ceria, the work function Φ varies with various factors, such as the origin of the sample and the nature of the atmosphere. However, the relative variation $\Delta\Phi$ of the work function could be found in Ref. (21) on cerium oxide films on Pt (111) during oxygen uptake. From the given work function values of bulk Pt (5.7 eV), of bulk Ce (2.9 eV), and the variation $\Delta\Phi$ obtained after oxidation of Ce into CeO_2, a value of Φ (CeO_2) of 4.5 eV could be calculated. The difference between Φ (Pd) (ca. 5.1 eV) and Φ (CeO_2) makes possible the electron transfer from the semiconductor to the metal as in the examples referenced above.

The electron enrichment of palladium persisted during the cooling from 773 to 423 K (Fig. 2) since σ (Pd/CeO_2) remains smaller than σ (CeO_2). A subsequent outgassing at 423 K caused an increase in $\sigma(CeO_2)$ and a decrease in σ (Pd/CeO_2) (Fig. 2). The slight increase of σ (CeO_2) by outgassing hydrogen at 423 K has to be ascribed to a slight dehydroxylation of the surface, which generates some additional anionic vacancies. For Pd/CeO_2, the outgassing of hydrogen produces the same effect, which would have also increased σ. However, there simultaneously occurs a reverse spillover and a stronger electron enrichment of the metal (3, 13), which both contribute to an overall decrease of σ for Pd/CeO_2. Similar behavior was observed for Ni/CeO_2 (3).

3. *In Situ* Conductivity Measurements during the Catalytic Total Oxidation of Propane

3.1. Conductivity Variations under the Reaction Mixture at 423 K

After the electrical equilibrium at 423 K was reached, Pd/CeO_2 was promptly outgassed and the stoichiometric reaction mixture ($5O_2 + 1C_3H_8$) corresponding to the reaction

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \qquad [10]$$

was introduced into the cell at a total pressure of 13.7 Torr with partial pressures of the reactants equivalent to those used in the catalytic tests. The conductivities of both CeO_2 and Pd/CeO_2 decreased by about one order of magnitude, indicating that ceria was partially reoxidized at 423 K by the oxygen of the reaction mixture. This reoxidation is in agreement with that observed for other systems such as Pt, Rh, and Ni/TiO_2 (13) investigated by electrical conductivity (13, 14) and microcalorimetry (22). In the case of Pd/CeO_2, it concerns simultaneously (i) the dissociative adsorption of oxygen on exposed surface palladium atoms,

$$Pd_s + 1/2\,O_2(g) \rightleftarrows Pd_s - O, \qquad [11]$$

and (ii) the partial reoxidation of ceria,

$$CeO_{2-x} + (x - \varepsilon)/2\,O_2 \rightleftarrows CeO_{2-\varepsilon}. \qquad [12]$$

The latter equation can be applied to both CeO_2 and Pd/CeO_2 and corresponds to a partial filling of anionic vacancies according to

$$1/2\,O_2(g) + V_0^+ + e^- \rightleftarrows O^{2-}(\text{surface}). \qquad [13]$$

The reoxidation of ceria is only partial, since the decrease in conductivity remains within one order of magnitude.

It should be underlined that the electron transfer to palladium (Eq. [9]) persisted, even in the presence of the reaction mixture, since σ (Pd/CeO_2) remained smaller than σ (CeO_2).

3.2. Electrical Conductivity Measurements during the Oxidation of Propane under Programmed Heating

Preliminary remark. The catalytic activity of the two platinum electrodes in the conductivity cell produced a negligible conversion of propane. Indeed a calculation of the ratio $R = n_s(Pd)/n_s(Pt)$ of the exposed surface atoms of palladium in the catalyst and of platinum in the electrodes was equal to 1.13×10^3.

The kinetics of *in situ* temperature programmed electrical conductivity variations (TPEC) of CeO_2 and of Pd/CeO_2 are presented in Fig. 3 and the corresponding Arrhenius diagrams in Fig. 4. Between ca. 423 K and 526 K, the electrical conductivity of Pd/CeO_2 varied very little,

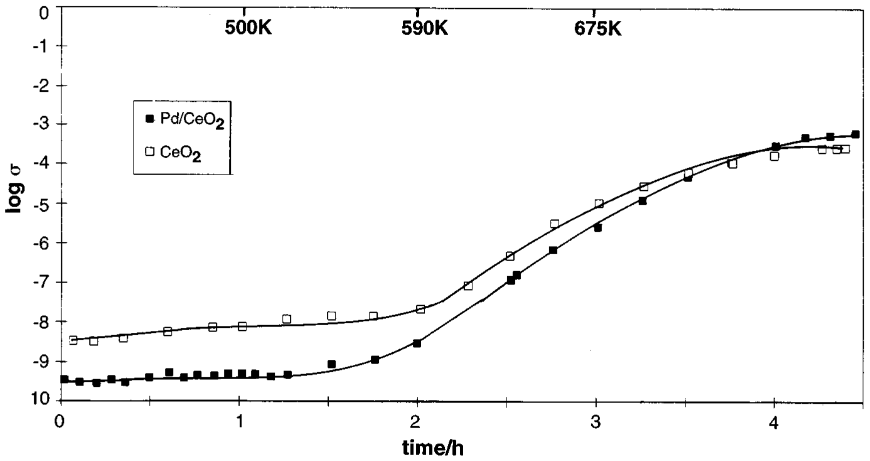

FIG. 3. Semilog plot of the variations in the electrical conductivity σ of Pd/CeO_2 and CeO_2 during the catalytic oxidation of propane.

with an apparent activation energy of 7.5 kJ/mol. From about 526 K, the electrical conductivity increased more markedly with $E_c = 70$ kJ/mol. The temperature of 526 K just corresponded to the beginning of the catalytic activity of Pd/CeO_2 (Fig. 1). This means the Pd/CeO_2 became catalytically active at the temperature where ceria became more conducting, i.e., more reducible.

From about 588 K, a second acceleration occurred for the temperature programmed electrical conductivity and, between 588 and 773 K, the activation energy of conduction increased to 253 kJ/mol, a value close to that observed for Pd/CeO_2 and CeO_2 during the TPR experiments.

$\sigma(CeO_2)$ remained higher than $\sigma(Pd/CeO_2)$ up to ca. 740 K, confirming the persistence of the electron enrichment of Pd particles which we suggest to occur below this temperature (Fig. 4). For naked ceria the activation energy of conduction was equal to 21 kJ/mol in the 423–588 K temperature range but reached 245 kJ/mol in the 588–703 K region; i.e., both solids had a common surface conduction mode in the latter temperature range. However, the activation energy of conduction of naked ceria decreased to 121 kJ/mol at 703 K, the temperature at which naked ceria became active in the total oxidation of propane (Fig. 1) and to which corresponds a change in the mode of surface electrical conduction.

4. Correlation between Electrical Conductivity and Surface Reactions

Dynamic activation energies of conduction measured during the temperature programmed reduction (TPR) or oxidation (TPO) of propane over Pd/CeO_2 provide information on surface reactions involving electron transfers in the solid or in catalytic processes. In this study, an activation energy of conduction of ca. 250 kJ/mol was observed in four different cases: (i) TPR under hydrogen for Pd/CeO_2 and

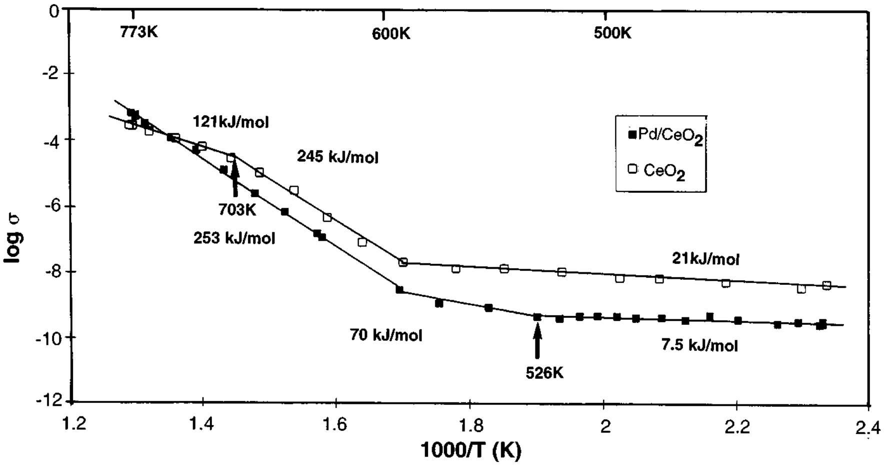

FIG. 4. Arrhenius diagrams $\log \sigma = f(1000/T)$ of the curves of Fig. 3 (the two vertical arrows indicate the initiation of the catalytic oxidation of propane on each solid: 526 K for Pd/CeO_2 and 703 K for CeO_2).

TABLE 1

Activation Energies of Conduction of Pd/CeO_2 and of CeO_2 under the Reaction Mixture for Different Temperature Domains and Corresponding Surface Reactions

Catalyst	Temperature range (K)	Dynamic activation energy of conduction E_c (kJ/mol)	Surface reaction concerned
Pd/CeO_2	423–526	7.5	No surface reactions involving electrons (E_c close to nil).
	526–588	70	Beginning of the catalytic reaction on Pd; beginning of the reduction of CeO_2, presumably by hydrogen spiltover from Pd after dissociative adsorption of propane.
	588–773	253	Reduction of CeO_2 by propane.
CeO_2	423–588	21	No surface reactions involving electrons.
	588–703	245	Stoichiometric reduction of CeO_2 by propane.
	703–773	121	Catalytic oxidation of C_3H_8 on CeO_2 (appearance of CO_2).

CeO_2 between ca. 300 and 773 K and (ii) TPO under the stoichiometric mixture of propane and oxygen in the temperature ranges 588–773 K or 588–703 K for Pd/CeO_2 and CeO_2, respectively. This value was obtained irrespective of the heating rate (between 1.4 and 8 K/min). Therefore, it can be inferred that the variations in the electrical conductivity resulted from the same origin, viz. the reduction of solids by a common reducing agent, namely hydrogen, in the four cases.

In the TPR experiments, the variations in σ have been ascribed to the formation of anionic vacancies by reduction of ceria by H_2 with the formation of H_2O (Eqs. [5] and [6]). Under the reaction mixture, hydrogen may be generated by dissociative adsorption of propane on Pd/CeO_2 or CeO_2 above ca. 526 and 588 K, respectively (Table 1). Over CeO_2, hydrogen would originate from the initial step of propane oxidation since it is known that CeO_2 is a total oxidation catalyst of light alkanes (23).

In the case of Pd/CeO_2, the metal surface is preferentially covered with chemisorbed oxygen from the reaction mixture at 423 K, because of the stronger adsorption energy of this gas on metal (22). As the temperature increases, the dissociative adsorption of propane on Pd can occur, presumably on the weakest adsorption sites. By analogy with previous studies concerning Pt/TiO_2 (20, 22), it is suggested that these weak sites are located at the metal-support perimeter. The resulting H atoms will therefore easily migrate by direct spillover onto the support and lead to the formation of OH groups which are precursors of anionic vacancies via dehydration:

$$2OH^- \rightarrow H_2O + V_0^+ + e^- + O^{2-}. \qquad [14]$$

Much lower values of E_c were observed in the temperature ranges for which the catalytic oxidation of propane prevailed over the creation of anionic vacancies (526–588 K for Pd/CeO_2 and 703–773 K for CeO_2) under the reaction mixture and it was observed that propane oxidation started at ca. 526 K over this catalyst (Fig. 1). Likewise, a conduction activation energy of 121 kJ/mol was registered over CeO_2 in the range where propane oxidation occurred.

These different behaviors are summarized in Table 1.

CONCLUSIONS

The present electrical conductivity study has enabled us to follow *in situ* the electrical behavior of a Pd/CeO_2 aerogel catalyst in the initial reduction treatment and in the final activity test (light-off determination) for the total oxidation of propane.

It was found that the order of magnitude of E_c is indicative of solid state or of surface catalytic reactions occurring on the solid.

Besides the confirmation of an intimate metal-support interaction, whose existence was pioneered by Schwab (24) and Solymosi (25), the main conclusions are the following:

— Ceria is reduced by hydrogen between 300 and 773 K with the formation of anionic vacancies; these defects are the source of free conduction electrons whose high Fermi level enables them to be transferred to Pd particles.

— During the whole catalytic run, despite the presence of oxygen, this electron transfer persists.

— The threshold temperatures of propane oxidation over Pd/CeO_2 (526 K) and over CeO_2 (703 K) correspond to changes in E_c during *in situ* temperature programmed electrical conductivity measurements.

— Palladium initiates the reaction at low temperature by breaking a C–H bond followed by the migration of H atoms onto the support.

— The most active sites of Pd/CeO$_2$ in the total oxidation of propane would be preferentially surface Pd atoms located at the Pd–CeO$_2$ interface; this would facilitate the localized hydrogen spillover of hydrogen onto the vicinal ceria surface anions and the subsequent formation of anionic vacancies.

— These anionic vacancies are refilled by gaseous oxygen, so that a redox process of ceria occurs in the neighborhood of Pd particles.

ACKNOWLEDGMENTS

The authors thank Dr. P. Pichat for fruitful discussions.

REFERENCES

1. See 2nd International Congress on Catalysis and Automative Pollution Control (CAPoC 2), *Stud. Surf. Sci. Catal.* **71**, (1991) and refs. therein.
2. Yao, Y. F. Y., *J. Catal.* **87**, 152 (1984).
3. Herrmann, J.-M., Romaroson, E., Tempere, J. F., and Guilleux, M. F., *Appl. Catal.* **53**, 117 (1989).
4. Hoang-Van, C., Harivololona, R., and Fayeulle, S., *in* "3rd International Congress on Catalysis and Automative Pollution Control (CAPoC 3), Brussels, Belgium, April 1994," Book of Preprints, Vol. 2, p. 119, 1994.
5. Hoang-Van, C., Pommier, B., Harivololona, R., and Pichat, P., *J. Non-Cryst. Solids* **145**, 250 (1992).
6. Hoang-Van, C., Harivololona, R., and Pommier, B., *Stud. Surf. Sci. Catal.* **91**, 435 (1995).
7. Duplan, J. L., and Praliaud, H., *Appl. Catal.* **67**, 32 (1991).
8. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Am. Chem. Soc.* **100**, 170 (1978).
9. Herrmann, J.-M., *in* "Catalyst Characterization; Physical Techniques for Solid Materials" (B. Imelik and J. C. Védrine, Eds.), p. 559. Plenum, New-York, 1994.
10. Van Oeffelen, D. A. G., Van Hooff, J. H. C., and Schuit, G. C. A., *J. Catal.* **95**, 84 (1985).
11. Caldararu, M., and Ionescu, N. I., *in* "Proceedings, 10th Internationational Congress on Catalysis, Budapest, 1992" (L. Guczi *et al.,* Eds.), p. 1879. Elsevier, Amsterdam, 1993.
12. Bjorklund, R. B., Odenbrand, C. U. I., Brandin, J. G. M., Andersson, L. A. H., and Liedberg, B., *J. Catal.* **119**, 187 (1989).
13. Herrmann, J.-M., *J. Catal.* **89**, 404 (1984).
14. Herrmann, J.-M., *J. Catal.* **118**, 43 (1989).
15. Ovenston, A., and Walls, J. R., *J. Phys. D.* **18**, 1859 (1985).
16. Bernal, S., Calvino, J. J., Cifredo, G. A., Laachir, A., Perrichon, V., and Herrmann, J.-M., *Langmuir* **10**, 717 (1994).
17. Harrison, B., Diwell, A. F., and Hallet, C., *Platinum Metals Rev.* **32**, 72 (1988).
18. Le Normand, F., Barrault, J., Breault, R., Hilaire, L., and Kiennemannn, A., *J. Phys. Chem.* **95**, 257 (1991).
19. Herrmann, J.-M., Disdier, J., and Pichat, P., *in* "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.,* Eds.), p. 27. Elsevier, Amsterdam, 1982.
20. Herrmann, J.-M., *in* "Strong Metal-Support Interactions" (R. T. K. Baker, S. J. Tauster, and J. A. Dumesic, Eds.), ACS Symp. Ser., Vol. 298, p. 200. 1986.
21. Hardacre, C., Roe, G. M., and Lambert, R. M., *Surf. Sci.* **326**, 1 (1995).
22. Herrmann, J.-M., Rumeau-Maillot-Gravelle, M., and Gravelle, P. C., *J. Catal.* **104**, 136 (1987).
23. Kennedy, E. M., and Cant, N. W., *Appl. Catal.* **75**, 321 (1991).
24. Schwab, G. M., *Adv. Catal.* **27**, 1 (1978).
25. Solymosi, F., *Catal. Rev. Sci. Eng.* **1**, 233 (1967).