

Characterization of Pd/ γ -Alumina Catalysts Containing Ceria

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The effects of adding CeO₂ to Pd/Al₂O₃ as a catalyst modifier were investigated by X-ray photoelectron spectroscopy and X-ray diffraction. Catalytic effects were demonstrated by using propane oxidation as a model reaction. It was found that CeO₂ promotes oxidation of Pd to PdO both with and without alumina. High-temperature reduction ($\approx 920^\circ\text{C}$) and the presence of Pd are required for the total conversion to bulk CeAlO₃ from CeO₂/Al₂O₃. Pd also assists in the oxidation of bulk CeAlO₃ to CeO₂ at elevated temperatures. In ambient air, Pd facilitates surface oxidation of CeAlO₃ to CeO₂, whereas surface Pd acquires an oxidation state between Pd⁰ and PdO. On Pd/Al₂O₃ the propane oxidation rate is found to be lowered by CeO₂ if the oxygen concentration exceeds that of the stoichiometric ratio. © 1988 Academic Press, Inc.

1. INTRODUCTION

Ceria (CeO₂) has been widely applied as an additive in automotive catalysts because of its abilities to store oxygen (1–4) and to improve dispersion of Pt (3, 4–6) and Rh (3, 4). Reduction of ceria on alumina in H₂ involves at least two reactions, namely, formation of nonstoichiometric cerium oxides (7–11) and cerium aluminate (CeAlO₃), depending on ceria loading (10–12). The aluminate remains stable in air at 600–800°C (10, 12). In a previous study, it was noted that in H₂ above 600°C dispersed ceria is completely transformed to CeAlO₃, while only partial conversion from ceria in the particulate phase to CeAlO₃ is observed even at 920°C (12). It was of interest to explore the effects of precious metals (PMs) on the formation of CeAlO₃ from ceria in the particulate phase resulting from PM-ceria interactions.

The purpose of this paper is to characterize chemical and structural changes due to interaction among Pd, ceria, and alumina by XPS (X-ray photoelectron spectroscopy)

and XRD (X-ray diffraction) under oxidizing and reducing conditions. Catalytic changes resulting from this interaction are demonstrated by using propane (C₃H₈) oxidation as a model reaction. Implications of this work in automotive catalysis are discussed. A parallel study involving Pt on CeO₂/Al₂O₃ is presented in a companion paper.

2. EXPERIMENTAL SECTION

2.1. Materials

CeO₂, CeO₂/Al₂O₃, and CeAlO₃/Al₂O₃ were prepared by the methods described previously (12). Samples that contain Pd were prepared by impregnation of CeO₂, CeO₂/Al₂O₃, and CeAlO₃/Al₂O₃ with aqueous solutions of Pd(NO₃)₂. The alumina support was obtained from Degussa (alumina-C) and had an initial BET area of 100 \pm 20 m²/g.

2.2. Propane Oxidation Activity

Measurements

Propane oxidation was studied with a flow reactor system equipped with a flame ionization detector (FID). The reactant mixture was composed of 1000 ppm C₃H₈ in N₂ with varying amounts of oxygen. The

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gas flow rate was set at ≈ 1500 ml/min. The catalyst weight was typically 0.2 g. All samples were reduced in 3% H_2 (in N_2) at $500^\circ C$ for 3 h and then cooled to room temperature before introduction of the reactant mixture.

2.3. XPS and XRD Measurements

XPS data were recorded on a Surface Science Laboratory SSX-100 XPS spectrometer with monochromatized $AlK\alpha$ X-rays. A $1000\text{-}\mu m$ spot size and 100-eV analyzer pass energy were typical for the analysis. Sample charging during the measurement was compensated by an electron flood gun operated at approximately 2 eV. The electron takeoff angle was 35° from the sample surface. Reduction of catalyst samples was carried out *in situ* in flowing H_2 at ≈ 10 ml/min in a reactor attachment (Physical Electronics) which can be operated at a maximum temperature of $600^\circ C$. Reduction of samples at higher temperatures was therefore carried out in a separate quartz reactor. These samples were exposed to ambient air while they were transferred to the reactor attachment for further treatment.

Binding energies (BE's) for samples containing alumina and ceria were referenced to $Al2p$ at 74.5 eV and $O1s$ at 529.0 eV, respectively. BE's of Pd^0 and PdO in reference materials were referred to the Fermi edge of Pd and $C1s$ at 284.6 eV, respectively.

XRD patterns were recorded on a Philips X-ray generator with a Debye-Scherrer camera. $CuK\alpha$ X-rays ($\lambda = 1.54178 \text{ \AA}$) were used as the X-ray source. The recorded film was step-scanned with a microdensitometer. Particle diameters of Pd and ceria were estimated by the Scherrer relationship,

$$t = 0.94\lambda/B \cos \theta, \quad (1)$$

where t is the particle diameter (\AA), λ is the wavelength of $CuK\alpha$ radiation, θ is the Bragg angle, and B is defined by

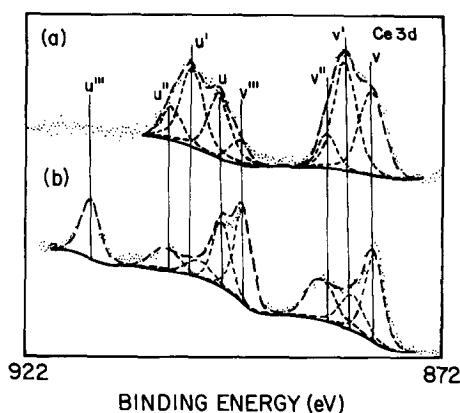


FIG. 1. $Ce3d$ XPS spectra. (a) $CeAl_2O_3$; (b) CeO_2 .

$$B^2 = B_m^2 - B_s^2, \quad (2)$$

where B_m is the measured line broadening for the sample and B_s is the instrumental line broadening measured using an $\alpha\text{-}Al_2O_3$ standard.

3. XPS ANALYSIS

XPS spectra of cerium compounds are known to exhibit rather complex features due to hybridization with ligand orbitals and fractional occupancy of the valence $4f$ orbitals (13–16). The $Ce3d$ XPS spectra of CeO_2 and 7 wt% $CeAlO_3/Al_2O_3$ are shown in Fig. 1. The complex spectrum of CeO_2 can be resolved into eight components by least-squares fitting with the assignment of each component defined in Fig. 1 (v 's represent the $Ce3d5/2$ contributions and u 's represent the $Ce3d3/2$ contributions). The theoretical basis for all the components has been reported in the literature (13, 15–16). The u''' peak, which arises from a transition of the $4f^0$ final state from the $4f^0$ initial state, has been used as a quantitative measure of the amount of Ce^{4+} (12). The u''' peak is absent from the $Ce3d$ spectrum of $CeAlO_3$. The absence of the u''' peak of the $Ce3d$ spectrum of $CeAlO_3$, compared to that of CeO_2 , is interpreted as the lack of the $4f^0$ configuration in the formal Ce^{3+} species.

It has been suggested that the $Ce3d$ spec-

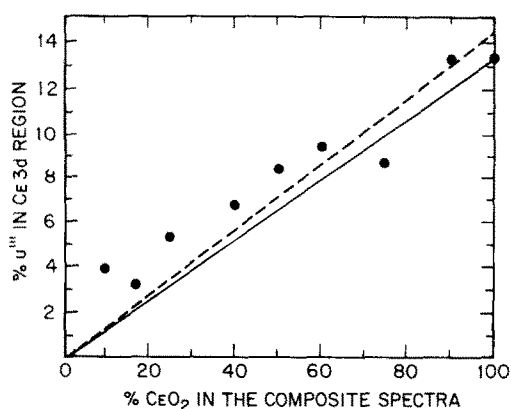


FIG. 2. Composite Ce3d spectra.

trum from partially oxidized Ce can be approximated as a linear combination of spectra recorded from the oxides (17). Assuming a uniform mixture of Ce^{4+} and Ce^{3+} , the relative intensity of u''' in the Ce3d region (Ce3d5/2 and Ce3d3/2) can be used to describe quantitatively the chemical state of Ce. Other peaks are also displayed to demonstrate the basis employed for estimating the total areas in the Ce3d region. However, to obtain a consistent estimate of the spectral background (nonlinear Shirley background), a small contribution of v''' is included in the Ce3d5/2 spectrum for CeAlO₃ even in the absence of the corresponding u''' in the Ce3d3/2 region. This incorporation of the v''' peak should not influence the total area in the Ce3d region. Thus, it should be valid to utilize the percentage u''' as a chemical identification for the amount of Ce^{4+} in the sample.

To translate the percentage u''' in the Ce3d region into percentage of Ce^{4+} , the following scheme was employed. A series of composite Ce3d spectra was synthesized by superimposing the spectra of CeO₂ and CeAlO₃ (Fig. 1) at various proportions with normalized peak areas. A plot of percentage u''' versus percentage CeO₂ (or 100% Ce^{4+}) for the composite spectra is shown in Fig. 2. The dashed line in Fig. 2 is obtained by a least-squares fit of the data points from the composite spectra through the origin,

whereas the solid line is a direct connection between end points derived from CeO₂ and CeAlO₃. This scheme is believed to provide a reasonable estimate for the percentages of CeO₂ and Ce^{3+} in the sample. The scatter of the points in Fig. 2 provides a measure for the accuracy of the spectra representatives. The relative error resulting from such a scheme is accordingly expected to be in the range of 10%.

4. RESULTS

4.1. XPS and XRD Results

4.1.1. Pd/Al₂O₃ and Pd/CeO₂. XPS results of clean Pd foil, PdO, Pd/Al₂O₃, and Pd/CeO₂ are summarized in Table 1. The Pd3d5/2 BE's obtained for Pd⁰ and PdO are in good agreement with published results (18–20) and are used to identify the chemical states of Pd on catalyst samples.

After calcination at 800°C, Pd on alumina at 1.2 and 6.8 wt% yields a Pd3d5/2 BE of ≈ 337.0 eV, which corresponds to that of PdO within experimental error (± 0.15 eV). Reduction of the sample containing 6.8 wt% Pd at 500°C produces Pd⁰ (BE = 334.9 eV). After reduction in H₂ at 920°C, followed by exposure to air at room temperature, XPS indicates that no substantial reoxidation of Pd⁰ occurs during exposure to ambient air.

A similar study was conducted on 0.6 wt% Pd/CeO₂. This sample has a Pd loading comparable to that of 6.8% Pd/Al₂O₃ on the basis of the amount of Pd per square meter surface area of the support. As in the case of Pd on alumina, calcination of 0.6 wt% Pd on CeO₂ at 800°C produces a Pd3d5/2 BE of 336.9 eV, which is the BE of PdO (see Table 1). Reduction of the sample *in situ* at 500°C results in formation of Pd⁰ on ceria (Pd3d5/2 = 335.1 eV), as found in the case of Pd on alumina. After a more severe reduction at 920°C, followed by exposure to ambient air, Pd yields the Pd3d5/2 BE of PdO (337.0 eV).

Thus, Pd reduced in H₂ at 920°C and then exposed to ambient air produces PdO on

TABLE 1
XPS Data of Pd Foil, PdO, Pd/Al₂O₃, and Pd/CeO₂

Sample	Treatment history	BE (eV) Pd3d5/2 ^a	Assignment
Pd foil	Sputtered clean	334.9	
PdO	As received	336.8	
1.2% Pd/Al ₂ O ₃	800°C calcined	337.0	PdO
6.8% Pd/Al ₂ O ₃	1. 800°C calcined	337.1	PdO
	2. 500°C reduced	334.9	Pd ⁰
	3. 920°C reduced, then exposed to air	335.0	Pd ⁰
0.6% Pd/CeO ₂	1. 800°C calcined	336.9	PdO
	2. 500°C reduced	335.1	Pd ⁰
	3. 920°C reduced, then exposed to air	337.0	PdO

^a BE references are defined in the text.

ceria, but Pd metal on alumina. This difference suggests that ceria promotes the oxidation of Pd in air and thus confirms a suggestion reported in the literature (23).

4.1.2. Pd-CeO₂/Al₂O₃. Pd3d XPS spectra of 4.5 wt% Pd on alumina containing 18.4 wt% CeO₂ are shown in Fig. 3. After calcination at 800°C, the supported Pd is

present mainly as PdO (Pd3d5/2 = 337.0 eV, Fig. 3a). Reduction at 920°C followed by exposure to air results in two different Pd species (Fig. 3b). The first species at 335.8 eV corresponds to a state between PdO and Pd⁰, while the second peak at a higher BE is probably attributable to Pd with chemisorbed oxygen (18).

To explore the nature of the Pd species at 335.8 eV, the sample was reduced at 500°C (see Fig. 3c). This reduction should reverse any surface oxidation which may have occurred during exposure to ambient air. The sample, reduced *in situ* at 500°C, gives a Pd3d5/2 BE of 334.8 eV, the BE of Pd⁰. A reduction at 500°C of a sample calcined at 800°C gives the same metallic Pd state (Pd3d5/2 = 335.0 eV) (Table 2). Since reduction of both the calcined and prerduced samples leads to the formation of Pd⁰, the presence of the Pd species at 335.8 eV on the 920°C prerduced sample must be due to oxidation of Pd⁰ on CeO₂/Al₂O₃ in ambient air. Compared to Pd supported on Al₂O₃, where no significant oxidation of Pd⁰ is seen after exposure to ambient air, ceria on alumina apparently promotes the Pd oxidation. As mentioned above, a similar result has been noted for Pd/CeO₂ in the absence of alumina, where Pd is completely oxidized to PdO in ambient air.

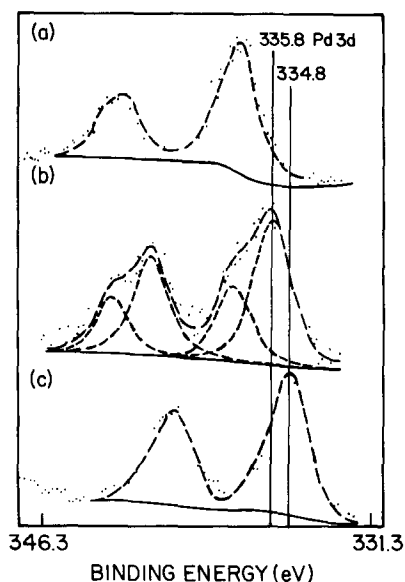


FIG. 3. XPS spectra of Pd-CeO₂/Al₂O₃ catalysts containing 4.5% Pd and 18.4% CeO₂. (a) Calcined at 800°C; (b) reduced at 920°C, exposed to air; (c) sample (b) reduced *in situ* at 500°C.

TABLE 2
 XPS Data for Pd–CeO₂/Al₂O₃

Sample	Treatment history	% <i>u</i> ^{'''}	BE (eV) Pd3d5/2 ^c
I. 16.2% CeO ₂ /Al ₂ O ₃	1. 800°C calcined	9.3(65) ^a	
	2. 920°C reduced/A ^b	3.4(23)	
	3. above, 500°C calcined	3.4(23)	
II. 9.2% Pd, 16.2% CeO ₂ /Al ₂ O ₃	1. 800°C calcined	10.3(72)	337.0
	2. 500°C <i>in situ</i> reduced	10.1(70)	335.0
	3. 920°C reduced/A	6.1(43)	335.6
	3a. above, <i>in situ</i> reduced at 500°C	0.0(0)	334.9
	3b. above, 600°C calcined	7.0(48)	337.3
III. 4.5% Pd, 18.4% CeO ₂ /Al ₂ O ₃	1. 800°C calcined	10.1(70)	337.0
	2. 500°C <i>in situ</i> reduced	10.1(70)	335.0
	3. 920°C reduced/A	4.4(32)	335.8
	3a. above, 500°C <i>in situ</i> reduced	0.0(0)	334.8
	3b. above, 500°C calcined	9.3(65)	336.9
IV. 0.9% Pd + 18.7% CeO ₂ /Al ₂ O ₃	1. 800°C calcined	—	337.1
	2. 920°C reduced/A	2.1(15)	335.5

^a Numbers in parentheses represent percentage of CeO₂ (Ce⁴⁺) in the Ce3d spectra, estimated on the basis of the dashed line in Fig. 2.

^b /A denotes that samples have been exposed to air at room temperature after the treatment.

^c Principal Pd3d5/2 peak.

Changes in the Ce chemistry, as measured by XPS analysis, are given in Table 2 and Fig. 4. In a previous study (12), we have noted that a ceria–alumina interaction results in a highly stable dispersed ceria in the Ce(III) state. The presence of this Ce(III) species, which is stable in air even at 800°C, lowers the total percentage *u*^{'''} in the Ce3d spectra and accounts for the fact that the Ce⁴⁺ contribution is always less than 100% as listed in Table 2. After calcination at 800°C, the percentages of the *u*^{'''} peaks amount to 9.3, 10.1, and 10.3%, for the samples containing 0, 4.5, and 9.2 wt% Pd, respectively. These percentages, corresponding to 65, 70, and 72% of Ce⁴⁺ (CeO₂), respectively, are constant within experimental error ($\pm 10\%$). Thus, according to XPS analysis, Pd does not appear to modify the chemistry upon calcination of CeO₂ on alumina.

After reduction at 920°C, followed by exposure to ambient air, the amount of Ce present as Ce⁴⁺ is found to increase with Pd loading (Figs. 4b–4d). The existence of

Ce⁴⁺ is deemed to be the result of surface oxidation of CeAlO₃ to CeO₂ in ambient air in the presence of Pd, on the basis of the following observations. Reduction *in situ* at 500°C of the sample prerduced at 920°C results in the absence of the *u*^{'''} peak (Fig. 4e), which is characteristic for the total conversion of surface CeO₂ to CeAlO₃. The complete conversion to bulk CeAlO₃ on alumina from CeO₂/Al₂O₃ after reduction at 920°C, which has been confirmed by XRD (Fig. 5b and Table 3), is the general result of ceria reduction in the presence of Pd at high temperatures ($\approx 920^\circ\text{C}$) and is discussed below.

This finding is supported by XPS data obtained after direct reduction at 500°C (Table 2). For 4.5 and 9.2% Pd on 18% CeO₂/Al₂O₃, the percentage *u*^{'''} remains essentially at the same value measured after calcination at 800°C and corresponds to $\approx 70\%$ Ce⁴⁺. The unchanged percentage of *u*^{'''} indicates that reduction at 500°C is not sufficient to form CeAlO₃. Analysis by XRD of these samples reduced *in situ* at 500°C re-

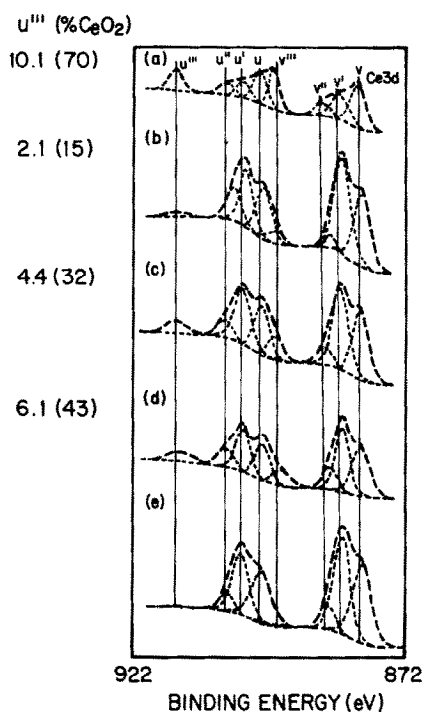


FIG. 4. XPS spectra of Pd-CeO₂/Al₂O₃. (a) 4.5% Pd and 18.4% CeO₂, calcined at 800°C; (b) 0.9% Pd and 18.7% CeO₂, reduced at 920°C; (c) 4.5% Pd and 18.4% CeO₂, reduced at 920°C; (d) 9.2% Pd and 16.2% CeO₂, reduced at 920°C; (e) reduction of sample (c) *in situ* at 500°C.

veals that Pd is present as Pd⁰ having a particle size of ≈15 nm, and Ce is in the form of CeO₂. Both XPS and XRD data lead to the conclusion that reduction at 500°C does not convert CeO₂/Al₂O₃ to CeAlO₃ for samples within the Pd concentration range used.

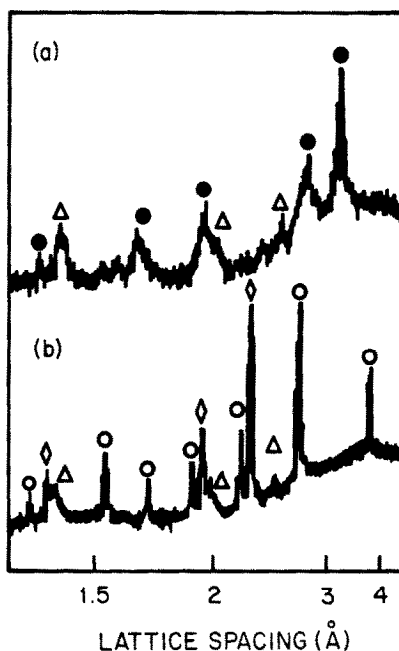


FIG. 5. X-ray powder diffraction of CeO₂/Al₂O₃ containing 9.2% Pd on 16.2% CeO₂/Al₂O₃. (a) Calcined at 800°C; (b) sample (a) reduced at 920°C. (Δ) γ-Al₂O₃; (●) CeO₂; (◊) CeAlO₃; (◊) Pd⁰.

Without Pd, even reduction at temperatures as high as 920°C for 2 h did not complete conversion to CeAlO₃ in the 16.6% CeO₂/Al₂O₃ sample (Table 2 and Fig. 6b). This result indicates that both high temperature and the presence of Pd are required for the total conversion of CeO₂ into CeAlO₃ under the conditions used. It follows from analyses by XRD (Table 3) that Pd and Ce on the reduced sample are present as Pd⁰ and CeAlO₃, respectively,

TABLE 3

X-ray Powder Diffraction for CeO₂/Al₂O₃ Containing Pd

Sample	Treatment history	Particle size (nm)		
		CeO ₂	CeAlO ₃	Pd
16.2% CeO ₂ /Al ₂ O ₃ , 9.2% Pd doped ^a	800°C calcined	8.2	—	—
	920°C reduced/A ^a	—	25.2	25.3

^a Sample has been exposed to air at room temperature after the treatment.

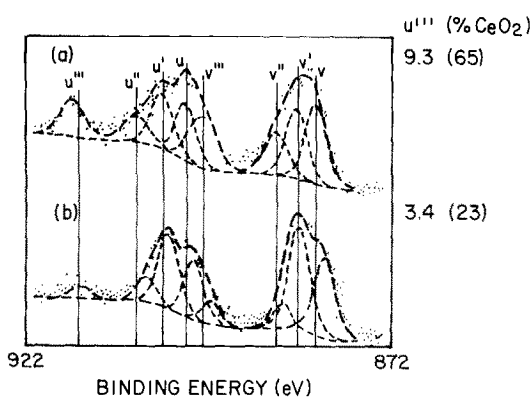


FIG. 6. XPS spectra of 16.6% $\text{CeO}_2/\text{Al}_2\text{O}_3$. (a) Calcined at 800°C ; (b) reduced at 920°C .

and both species exist as small particles (≈ 25 nm).

CeAlO_3 , obtained by reduction of 18% $\text{CeO}_2/\text{Al}_2\text{O}_3$ at 920°C , is reoxidized to CeO_2 in ambient air (compare samples II and III under conditions (3a) and (3b) in Table 2). The oxidation is induced by Pd and does not occur without the metal (see sample I in Table 2). Meanwhile, Pd itself is partially oxidized, as noted previously. This result is based on XPS analysis. On the other hand, XRD gives no indication of any oxidation of either CeAlO_3 or Pd. The chemical state measured by XPS after oxidation at room temperature is therefore attributed to poorly crystallized CeO_2 on the alumina surface.

4.1.3. $\text{Pd-CeAlO}_3/\text{Al}_2\text{O}_3$. The results reported above are confirmed further by the

use of cerium aluminate on alumina as a support for Pd. Data from XPS measurements of 10% CeAlO_3 on Al_2O_3 are summarized in Table 4. After 500°C calcination of a sample without Pd, virtually no change of u''' in the $\text{Ce}3d$ region is detected (within 10% error). However, when Pd is present in the sample, calcination at 500°C results in significant oxidation of CeAlO_3 to Ce^{4+} , evident from a substantial increase in u''' . The extent of oxidation is the same (65%) for samples doped with 5 and 10 wt% Pd. Moreover, in both cases, Pd is present as PdO (Pd3d5/2 BE of $\approx 336.8 \pm 0.2$ eV). Reduction at 500°C of the calcined sample containing 5 wt% Pd restores the CeAlO_3 phase only partially (4.7% u''' or 35% Ce^{4+} in the sample), while Pd is reduced to its metallic state. The incomplete conversion of CeO_2 to CeAlO_3 after the reduction corroborates the conclusion that reduction of bulk CeO_2 , even in the presence of Pd, requires a temperature above 500°C .

The bulk structure of 10% CeAlO_3 on Al_2O_3 was also examined by XRD. Results are shown in Figs. 7 and 8. Diffraction lines of samples without Pd, either fresh or calcined at 500°C , are attributable to CeAlO_3 and $\gamma\text{-Al}_2\text{O}_3$. However, as shown in Fig. 8, samples doped with 1 or 5 wt% Pd (Pd/ CeO_2 molar ratios are 0.16 and 0.81, respectively) and calcined at 500°C contain, in addition, CeO_2 . As the Pd loading is increased to 10 wt% Pd (atomic Pd/Ce = 1.6), the diffraction lines of CeAlO_3 disappear al-

TABLE 4

XPS Data of 10% $\text{CeAlO}_3/\text{Al}_2\text{O}_3$ Containing Pd

Sample	Treatment history	% u'''	BE (eV) Pd3d5/2
Undoped	1. As prepared ^b	3.4(23) ^a	
	2. 500°C calcined	4.4(32)	
5% Pd doped	1. 500°C calcined	9.3(65)	337.0
	2. 500°C <i>in situ</i> reduced	4.7(35)	335.0
10% Pd doped	1. 500°C calcined	9.4(66)	336.7

^a Numbers in parentheses represent percentage of Ce^{4+} in the sample, as estimated on the basis of the correlation curve in Fig. 2.

^b Prepared by reduction at 1000°C of 10% $\text{CeO}_2/\text{Al}_2\text{O}_3$ for 80 h.

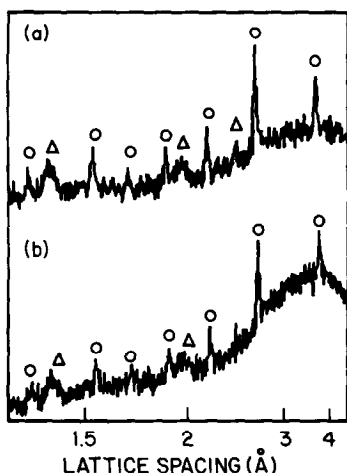


FIG. 7. X-ray powder diffraction of 10% $\text{CeAlO}_3/\text{Al}_2\text{O}_3$. (a) As prepared; (b) sample (a) calcined at 500°C . (○) CeAlO_3 ; (Δ) $\gamma\text{-Al}_2\text{O}_3$.

together (Fig. 8c). It appears therefore that complete oxidation of bulk CeAlO_3 requires an amount of Pd which is not less than the amount of Ce in the sample.

No diffraction lines associated with Pd are detected in any of the oxidized samples (Figs. 8a–8c). An explanation is given by the fact that Pd is present as dispersed PdO (less than ≈ 5 nm) on alumina. As expected, reduction of the same sample at 920°C restores the CeAlO_3 phase completely (Fig. 8d), while Pd becomes detectable as Pd^0 with a particle size of ≈ 35 nm (Table 5).

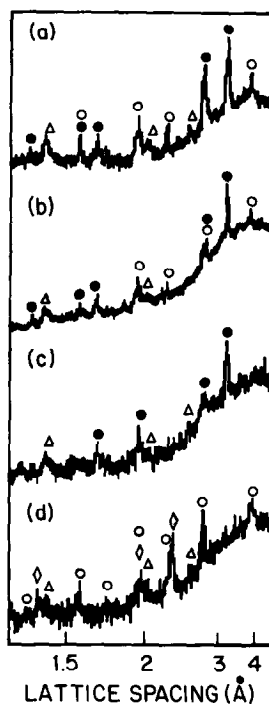


FIG. 8. X-ray powder diffraction of Pd on 10% $\text{CeAl}_2\text{O}_3/\text{Al}_2\text{O}_3$. (a) 1% Pd, calcined at 500°C ; (b) 5% Pd, calcined at 500°C ; (c) 10% Pd, calcined at 500°C ; (d) 10% Pd, reduced at 920°C . (Δ) $\gamma\text{-Al}_2\text{O}_3$; (●) CeO_2 ; (○) CeAlO_3 ; (◊) Pd^0 .

It is apparent from these results that Pd assists in the oxidation of CeAlO_3 to CeO_2 . Unlike the oxidation of CeAlO_3 in the presence of Pd at room temperature, where only surface oxidation is evident, calcina-

TABLE 5
X-Ray Powder Diffraction Data for 10% $\text{CeAlO}_3/\text{Al}_2\text{O}_3$

Sample	Treatment history	Particle size (nm)		
		CeO_2	CeAlO_3	Pd
Undoped	As prepared	—	22.2	—
	500°C calcined	—	19.1	—
1% Pd doped	500°C calcined	18.8	15.5	—
5% Pd doped	500°C calcined	19.6	5.5	—
10% Pd doped	500°C calcined	22.0	—	—
10% Pd doped	920°C reduced/ A^a	—	18.5	35.7

^a Sample has been exposed to air at room temperature after the treatment.

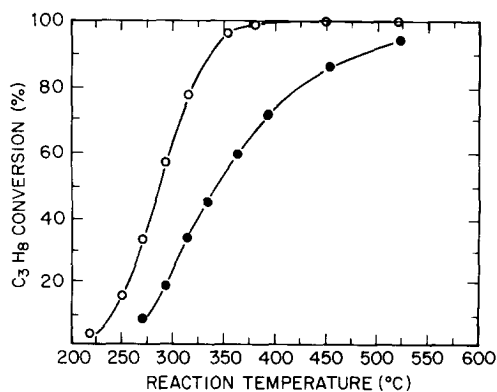


Fig. 9. Propane oxidation on 10 wt% Pd/ γ -Al₂O₃. Feed gas: 1000 ppm C₃H₈ and 2.0% O₂. (○) Undoped; (●) doped with 10 wt% CeO₂.

tion at 500°C results in bulk oxidation of CeAlO₃ to CeO₂. This conclusion is based on both XPS and XRD.

4.2. Propane Oxidation over Pd-CeO₂/Al₂O₃ Catalysts

Propane oxidation by oxygen was used in this study as a model reaction to probe catalytic additive effects of ceria on Pd/Al₂O₃. The reaction mixture at the catalyst inlet consists of 1000 ppm C₃H₈ and 2% O₂ in N₂; i.e., the oxygen concentration is four times that required for a complete oxidation of propane to CO₂ and H₂O. Typical reaction curves of propane oxidation on 10% Pd/

Al₂O₃ with and without 10% CeO₂ added are given in Fig. 9. The temperature at 50% propane conversion, T_{50} , was chosen as an activity index. As shown in Fig. 9, addition of ceria to 10 wt% Pd on Al₂O₃ increases T_{50} from 288 to 343°C; i.e., it lowers the catalyst activity. Thus, the presence of ceria can deactivate Pd/Al₂O₃ catalysts to some extent.

Reaction curves measured with stoichiometric feed gas (C₃H₈: O₂ = 1 : 5) are shown in Fig. 10. Again, the added 10 wt% ceria lowers the catalyst activity. The effect, however, is smaller at the stoichiometric oxygen concentration, characterized by an increase in T_{50} from 304 to 329°C.

The influence of oxygen concentration on the ceria effect is illustrated further by results shown in Fig. 11. In this case reaction isotherms were measured at 350°C and oxygen levels from 0.25 to 4%. Clearly, in the absence of ceria, propane oxidation over 10% Pd/Al₂O₃ is unaffected by the feed gas composition in the range given. On the other hand, in the presence of ceria, an abrupt decrease in conversion occurs when conditions are changed from stoichiometric to oxidizing. Above 2% oxygen no further change in activity takes place. It should also be noted that at 0.25% oxygen the rate of propane oxidation over 10% Pd/Al₂O₃ is the same with and without ceria. Only

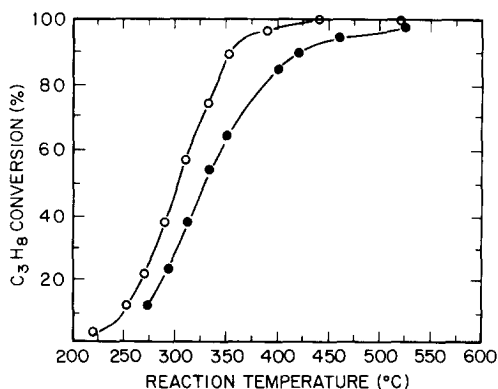


Fig. 10. Propane oxidation on 10 wt% Pd/ γ -Al₂O₃. Feed gas: 1000 ppm C₃H₈ and 0.5% O₂. (○) Undoped; (●) doped with 10 wt% CeO₂.

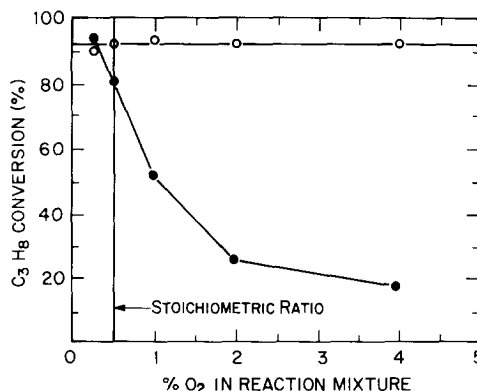


Fig. 11. Propane oxidation on 10 wt% Pd/ γ -Al₂O₃. C₃H₈ concentration in feed gas: 1000 ppm. Reaction temperature: 350°C. (○) Undoped; (●) doped with 10 wt% CeO₂.

when the oxygen concentration exceeds the stoichiometric ratio does the addition of ceria to Pd/Al₂O₃ cause catalyst deactivation. The kinetic data, together with results derived from XPS and XRD, indicate that the presence of ceria modifies the Pd chemistry under oxidizing conditions.

5. DISCUSSION

The experimental results presented in this paper can be summarized as follows:

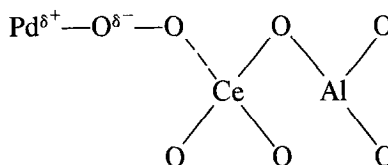
1. With or without alumina, ceria promotes the oxidation of Pd to PdO. As a result, addition of CeO₂ to Pd/Al₂O₃ retards the catalytic oxidation rate of propane over palladium for reactant mixtures which exceed the stoichiometric O₂/C₃H₈ ratio, in which palladium is presumably in its oxidized state.

2. Upon reduction at high temperatures, palladium assists in the formation of bulk CeAlO₃ from CeO₂/Al₂O₃. Also, Pd catalyzes bulk oxidation of CeAlO₃ at elevated temperatures.

3. Palladium assists in the surface oxidation of CeAlO₃ in ambient air, whereas surface Pd is partially oxidized to a state between Pd⁰ and PdO.

On the basis of these observations, it is apparent that cerium oxides and palladium are subject to mutual interaction. Such an interaction has been proposed by Sass *et al.* (23, 26) on the basis of EPR and reaction activity measurements in which an active O₂⁻ species has been identified.

According to the XPS data in this study, surface oxidation of CeAlO₃ by Pd may also entail an intermediate species containing Pd⁺O₂⁻. Coordinately unsaturated CeAlO₃ adsorbs oxygen in air to form O₂⁻ species (8), which may be stabilized by forming a surface species with palladium. Thus, a tentative model is derived to explain the experimental observations. The model is based on the structure



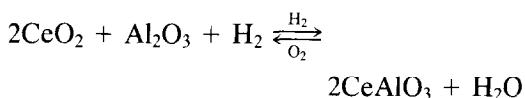
In this proposed structure of the oxidized surface species, Pd is in a state between Pd⁰ and PdO, whereas cerium is in its tetravalent state. This surface complex can be reduced at mild temperatures to form Pd⁰ and CeAlO₃, while oxidation results in splitting of the O₂⁻ species to form bulk PdO and CeO₂. It appears that palladium plays an important role in both formation and oxidation of CeAlO₃. Adsorption of oxygen results in the formation of O₂⁻ (8, 26, 27) that is stabilized in the coordination sphere of the palladium and cerium ions (22, 23) and leads to the reversible formation of CeAlO₃ from CeO₂/Al₂O₃.

Mutual influences between Pd and ceria are also reflected in the propane oxidation. Strong dependence of the oxidation rate of propane on oxygen concentration over Pd/Al₂O₃ containing ceria is interpreted as surface chemical changes of Pd by ceria under oxidizing conditions. As shown previously, under oxidizing conditions, Pd is converted to PdO in the presence of ceria. The formation of PdO is accompanied by a lower propane oxidation rate, a result which is consistent with conclusions published earlier from this laboratory (2, 25). Therefore, from a practical standpoint in automotive catalysis, the air/fuel ratio should be adjusted near the stoichiometric ratio when Pd and ceria are both present. This allows a more efficient use of Pd without losing other important functions that ceria can provide, such as stabilization of γ -Al₂O₃, dispersion of Pt and Rh, and oxygen storage.

6. CONCLUDING REMARKS

In summary, it can be stated that a complex interaction among ceria, palladium, and alumina clearly influences the revers-

ible reaction



This interaction is detected after reduction at 920°C, when the formation of bulk aluminate is catalyzed in the presence of Pd; during the reverse reaction, the oxidation of bulk aluminate at 500°C is also catalyzed by Pd. A distinct modification of Pd in ambient air was demonstrated by an oxidation state between Pd⁰ and PdO.

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