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LETTERS TO THE EDITOR

Rietveld Refinement of the Structure of CeOCl Formed in Pd/CeO_2 Catalyst: Notes on the Existence of a Stabilized Tetragonal Phase of La_2O_3 in La–Pd–O System

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A structure of CeOCl formed during the synthesis of Pd/CeO_2 catalyst from $PdCl_2$ and CeO_2 was refined by the Rietveld method from the X-ray powder diffraction data. CeOCl has a PbFCl-type structure with tetragonal space group *P4/nmm*; $a = 4.0785(1)$ Å, $c = 6.8346(3)$ Å. It is shown that a phase found and refined by Guru Row *et al.* (*J. Solid State Chem.* **95,** 224, 1991) described as a palladium stabilized tetragonal phase of La_2O_3 seems to be LaOCl, the compound with a structure isomorphous with CeOCl. © 1992 Academic Press, Inc.

Le Normand *et al.* (*1*) reported that during synthesis of Pd/rare-earth oxide catalysts (*RE* = La, Pr, Nd, and Tb) by impregnation of the oxide with $Pd(NH_3)_4Cl_2$ precursor the *RE*OCl compounds with a tetragonal structure described by Templeton and Dauben (*2*) were formed. We observed the growth of a similar CeOCl phase when preparing Pd/CeO_2 catalyst by a different, liquid-phase method and $PdCl_2$ precursor.

A sample of Pd/CeO_2 catalyst was prepared by evaporating and drying (at 350 K) a mixture of $PdCl_2$ solution and a colloidal dispersion of CeO_2 in diluted acetic acid. The sample contained 9 wt% Pd and 8 wt% Cl. It was reduced under hydrogen flow (p = 1 atm) at 900 K for 20 hr, which decreased the content of Cl to 7 wt%.

Preliminary X-ray powder diffraction studies showed the existence of three phases: CeO_2, CeOCl, and Pd. The quality of the diagrams was not as good as usual for catalysts of such a type. Only a part of the material was crystalline and contributed to the diffraction. The phases possessed crystallites of different sizes.

The final, room-temperature X-ray diffraction data were collected on a D-5000 diffractometer (Bragg–Brentano geometry, Cu*Kα* radiation). The details of the refinement, performed with DBWS-9006PC program (*3*), are collected in Table I and shown in Fig. 1. Generally, the results are consistent with those reported in (*2*) except for minor discrepancies in the lattice parameters and the atomic positions.

Guru Row *et al.* (*4*) attempted to prepare La_2PdO_4 by heating a stoichiometric mix-

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TABLE I

DETAILS OF THE RIETVELD REFINEMENT PERFORMED ON THE SAMPLE OF Pd/CeO_2 CATALYST CONTAINING CeO_2, CeOCl, AND Pd

2Θ range (deg):	10.00–90.00
Step-scan size (deg):	0.02
Number of points:	4001
Profile shape:	Pearson VII
Number of profile parameters:	14
Number of structure parameters:	15
CeOCl:	Space group: *P4/nmm; Z* = 2 a = 4.0785(1) Å, c = 6.8346(3) Å Ce: 2(c) 0.25, 0.25, 0.175(0); B = 0.71(2) $Å^2$ O: 2(a) 0.25, 0.75, 0; B = 1.56(70) $Å^2$ Cl: 2(c) 0.25, 0.25, 0.629(1); B = 1.65(30) $Å^2$ Scale factor: 0.577(40) $\times 10^{-3}$ Half-width coefficients (U, V, W): 0, −0.01245(659), 0.06313(264) Profile shape parameter m: 1.41(5)
CeO_2:	Space group: *Fm*3*m* a = 5.4124(1) Å Ce: 4(a) 0, 0, 0; B = 0.29(2) $Å^2$ O: 8(c) 0.25, 0.25, 0.25; B = 1.82 (27) · $Å^2$ Scale factor: 0.334(2) $\times 10^{-3}$ Half-width coefficients (U, V, W): 0, 0.02973(44), 0.43123(500) Profile shape parameter m: 1.25(2)
Pd:	Space group: *Fm*3*m* a = 3.9079(1) Å Pd: 4(a) 0, 0, 0; B = 1.28(15) $Å^2$ Scale factor: 0.296(7) $\times 10^{-3}$ Half-width coefficients (U, V, W): 0, 0, 0.13690(581) Profile shape parameter m: 1.49(3)
Discrepancy factors:	$R_p = 0.072$, $R_{wp} = 0.097$, R_B(CeOCl) = 0.073 $S = 1.88$, D-$W\ d = 1.48$

Note. Half-widths are calculated according to the formula $HW = \sqrt{(U \tan^2\Theta + V \tan\Theta + W)}$.

ture of La_2O_3 and $PdCl_2$ at 1050 K in air for 20 hr. As a result, they obtained a mixture of PdO and a second phase, which they described as a palladium stabilized tetragonal form of La_2O_3. The tetragonal phase with a = 4.13 Å and c = 6.90 Å could be refined in the *P4/mmm* space group, but the differences in the I_{obs}-I_{calc} values for several lines remained somewhat large (see (*4*) Fig. 1). In our opinion this phase is in fact LaOCl—a phase with the structure of the same type as CeOCl (*5*). Figure 2 compares three powder diagrams: (a) generated according to the numerical data derived from the measurement of Guru Row *et al.* (here, some reflections excluded from the refinement by Guru Row *et al.* were left in the diagram; intensity of the 102 reflection at 2Θ = 34.20 was lowered because of the contribution of PdO); (b) calculated according to the model of "stabilized lanthanum oxide"; and (c) calculated for LaOCl, according to the data from (*5*).

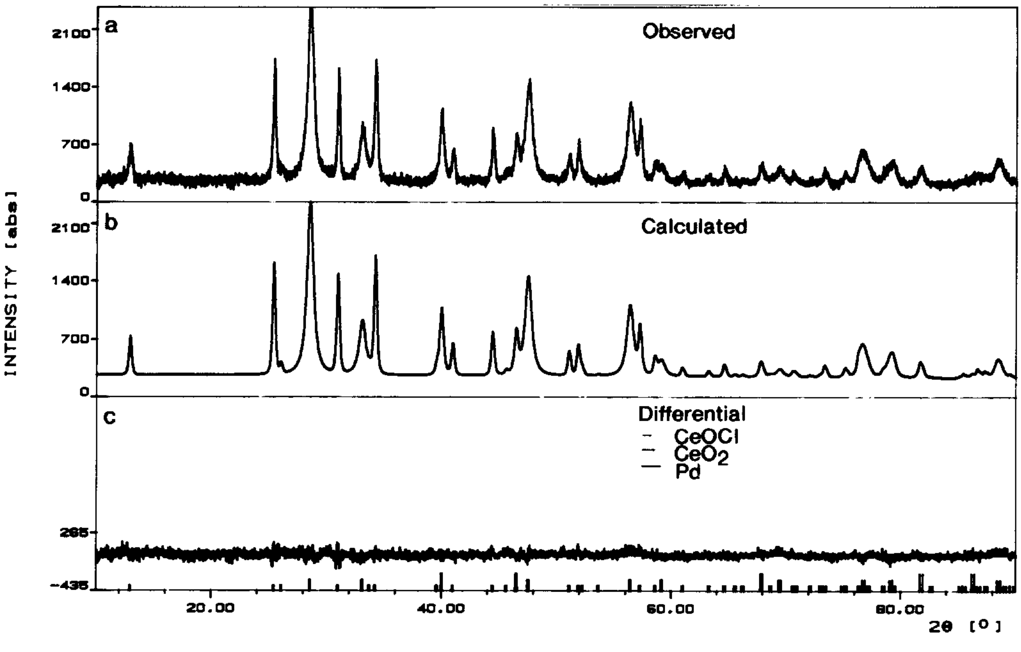

FIG. 1. Results of the Rietveld refinement performed on the sample of Pd/CeO$_2$ catalyst containing CeO$_2$, CeOCl, and Pd. (a) Measured diagram, (b) calculated diagram, (c) differential diagram and peak positions.

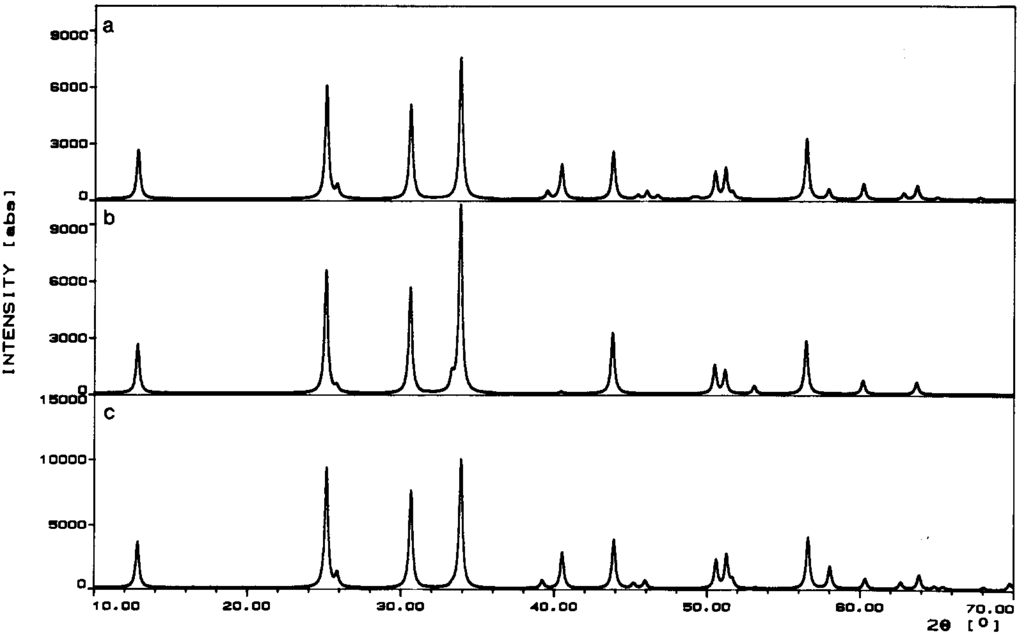

FIG. 2. (a) Powder diagram of "stabilized lanthanum oxide" generated according to the numerical data derived from the measurement of Guru Row *et al.* (*4*). (b) Diagram calculated according to the model of Guru Row *et al.* (c) Calculated diagram of LaOCl according to the data from (*5*).

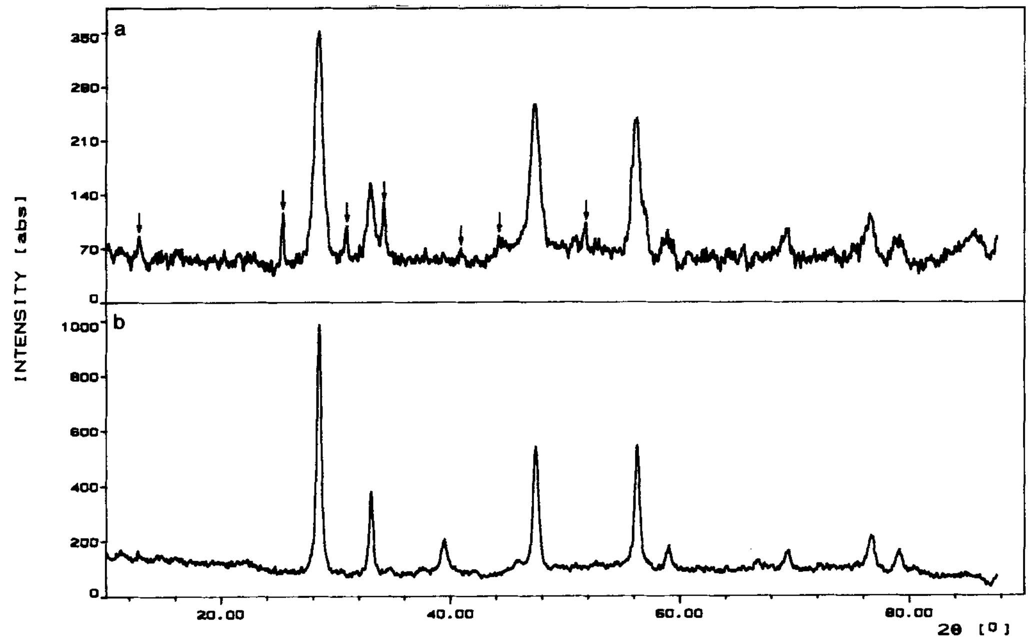

FIG. 3. Powder diagrams for the control samples: (a) Cl/CeO_2, (b) Pd/CeO_2 (Cl-free) reduced under hydrogen at 900 K for 20 hr. Reflections from CeOCl are indicated by arrows.

It is seen that the consistency between (a) and (c) is sufficiently good and much better than that between (a) and (b).

Guru Row *et al.* reported similar results obtained for the sample prepared in a different way, namely, by the decompostion of mixed La and Pd nitrates. Naturally, because of the lack of Cl, in such a case LaOCl could not be created. However, the authors did not present any diagram of this sample.

In order to explain this discrepancy, we prepared two control samples: (a) containing Cl and CeO_2 (without Pd) and (b) containing Pd and CeO_2 (without Cl). The Cl/CeO_2 sample (a) was obtained by impregnation of CeO_2 with HCl, whereas the Pd/CeO_2 (Cl-free) sample (b) was obtained by the liquid method described earlier, but by using Pd nitrate solution instead of $PdCl_2$ solution. Both samples were reduced under hydrogen flow at 900 K for 20 hr; the resulting X-ray powder diagrams are shown in Fig. 3. It is seen that in the Cl/CeO_2 sample a small amount of CeOCl is formed (Fig. 3a). It proves that Pd is not necessary for the "palladium stabilized cerium oxide" to be formed, although it may catalyze the CeO_2–Cl reaction. In the absence of Cl, only CeO_2 and Pd reflections occur (Fig. 3b). According to these results, a mistake of Guru Row *et al.* seems to be evident. It is also worth noting that, consequently, the "palladium stabilized neodymium oxide" mentioned by Guru Row *et al.* is probably NdOCl.

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Postscript

Guru Row *et al.* have since found that the tetragonal phase was mainly due to the presence of LaOCl. They were led to believe that they had synthesized a new La_2O_3 phase since they obtained the same X-ray diffraction pattern with the product of the reaction of La and Pd nitrates. Unfortunately, the Pd nitrate that they used contained $PdCl_2$ as the main constituent. Guru Row *et al.* now find that many rare-earth oxychlorides, *Ln*OCl (*Ln* = La, Nd, Sm, . . .), are readily prepared by the reaction of the rare-earth oxide with $PdCl_2$ at 1050 K.

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