Crystal Structure of Partially Pd²⁺-Exchanged Zeolite X Dehydrated in Oxygen at 400 °C. Formation of Linear Pd₂O₃ Clusters Proposed To Be HO−Pd^{IV}−O−Pd^{IV}−OH in (Pd²⁺)₁₄(HOPdOPdOH⁴⁺)₈(Na⁺)₃₂−Si₁₀₀Al₉₂O₃₈₄

Seok Hee Lee and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

Karl Seff*

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

Received: August 31, 1999; In Final Form: December 8, 1999

The crystal structure of partially Pd²⁺-exchanged zeolite X, dehydrated at 400 °C in a flowing O₂ stream (a = 24.982(4) Å), has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at 21(1) °C. The crystal was first Pd²⁺-exchanged in a flowing stream of 0.05 M aqueous Pd(NH₃)₄Cl₂ for 3 days. After dehydration at 400 °C in flowing oxygen, the crystal was evacuated at 21(1) °C and 2 × 10⁻⁶ Torr for 2 h. The structure was refined to the final error indices R_1 = 0.070 and R_2 = 0.051 for the 196 reflections for which $I > 2\sigma(I)$. In this structure, Pd²⁺ ions are found at four crystallographic sites: Na⁺ ions fill just one, and nonframework oxygens are found at two. Eight Pd²⁺ ions and eight O²⁻ ions fill the 16 double six-oxygen ring (D6R) centers (site I) per unit cell; this interpretation of the electron density at site I behaves well in least-squares refinement. Each of these Pd²⁺ ions is octahedrally coordinated by framework oxygens. Sixteen Pd⁴⁺ ions at site I′ (Pd−O = 2.103(13) Å) lie in six-ring planes. With the eight oxide ions at site I at central positions and 16 more teriminal, they form eight linear O−Pd−O−Pd−O clusters along 3-fold axes per unit cell. Each passes through the center of a D6R and extends into its two adjacent sodalite cavities. Considering bond lengths and charge balance, it is proposed that they are [HO−Pd^{IV}−O−Pd^{IV}−OH]⁴⁺ clusters with O−Pd−O−Pd−O linear. Thirty-two Na⁺ ions fill site II and are recessed 1.03(1) Å into the supercage from the single six-ring plane (Na−O = 2.258(11) Å). About two Pd²⁺ ions at another site I′ (Pd−O = 2.371(11) Å) are displaced 1.11 Å from six-ring plane into sodalite cages. About four Pd²⁺ ions lie at site III′ in the supercage (Pd−O = 2.16(5) Å).

Introduction

The group VIII transition metals, Ni, Pd, and Pt, have been extensively studied because of their pronounced catalytic activity, in zeolites and otherwise.[1−3]

The study of the redox properties of supported metal particles can help in understanding the mechanisms of metal dispersion and sintering, which are important in industrial catalysis. Very small metal particles supported on Y-type zeolites may be oxidized to exchangeble cations rather than to metal oxide. Thus, silver and copper particles can be reoxidized into cations by heating the reduced Cu−Y and Ag−Y zeolites in oxygen.[4,5]

The structure of a Pd−Y zeolite was studied in situ under dynamic conditions during the course of various treatments performed in the controlled atmosphere furnace of an X-ray camera.[6] A complete description of the palladium positions was given as a function of O₂ activation at various temperatures. Its results may be summarized as follows. At temperatures below 250 °C, supercage Pd(NH₃)₄²⁺ ions lose ammonia to form Pd-(NH₃)₂²⁺ ions coordinated to lattice oxygen atoms. At higher temperatures, these ions decompose to Pd(NH₃)²⁺ or Pd²⁺, which move into the sodalite cages, where they are stabilized by electrostatic interactions and by higher coordination to framework oxygen atoms.[7−9] This is attributed to the higher negative charge density in this cavity.[8] The reduction of the palladium species by H₂ occurs at a lower temperature when

they are located in supercages, a higher temperature when they are in sodalite cages.[8,9] Reduction in the sodalite cages results in the formation of isolated atoms that migrate into the supercages.[7,9] In the case of Na−X, the decomposition of the Pd(NH₃)₄²⁺ complex in O₂ or air gives a small amount of PdO particles, characterized by EXAFS, in addition to Pd²⁺ ions coordinating normally to framework oxygen atoms. The Pd²⁺ ions are reduced to small Pd⁰ particles (perhaps including dimers) upon treatment with H₂ at room temperature.[10]

This work was done to investigate the cation distribution in the crystal structure of fully dehydrated partially Pd²⁺-exchanged zeolite X. Dehydration was done in oxygen to prevent Pd²⁺ from being reduced by H₂O or by oxygens of zeolite framework, both of which could damage the crystal by loss of framework oxygen.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry Na₉₂Si₁₀₀Al₉₂O₃₈₄, were prepared in St. Petersburg, Russia.[11] One of these, a colorless octahedron about 0.2 mm in cross-section was lodged in a fine Pyrex capillary. Ion exchange was accomplished by allowing 0.05 M Pd(NH₃)₄Cl₂ (Alfa Co. 99.998%) to flow past the crystal at the velocity of 1.0 cm/s for 3 days. The crystal was then dehydrated at 400 °C for 2 days in a flowing stream (790 Torr) of oxygen gas. Thereafter

Crystal Structure of Pd²⁺-Exchanged Zeolite X

J. Phys. Chem. B, Vol. 104, No. 11, 2000 **2491**

TABLE 1: Positional, Thermal, and Occupancy Parameters[a] for $(Pd^{2+})_{14}(HOPdOPdOH^{4+})_8(Na^+)_{32}-X$

atom	Wyc. pos	site	x	y	z	U_{iso}	occupancy[b] varied	fixed
Si	96(g)		−518(2)	1249(2)	354(2)	163(11)		96
Al	96(g)		−543(2)	374(2)	1240(3)	218(13)		96
O(1)	96(g)		−1096(5)	−7(7)	1060(5)	499(49)		96
O(2)	96(g)		−33(6)	−62(6)	1465(4)	241(33)		96
O(3)	96(g)		−334(4)	706(6)	680(6)	276(40)		96
O(4)	96(g)		−643(5)	762(6)	1802(7)	549(43)		96
Pd(1)	16(c)	I	0	0	0	40(15)	8.3(1)	8
Pd(2)[c]	32(e)	I′	387(2)	387(2)	387(2)	551(23)	16.3(3)	16
O(5)	16(c)		0	0	0	40(15)	7.7(1)	8
O(6)	32(e)		866(1)	866(1)	866(1)	356(152)	15.8(3)	16
Pd(3)	32(e)	I′	607(6)	607(6)	607(6)	385(72)	2.7(2)	2
Pd(4)	96(g)	III′	−185(19)	859(21)	4209(19)	468(164)	3.6(3)	4
Na(1)	32(e)	II	2296(3)	2296(3)	2296(3)	136(41)	33.1(2)	32

[a] Space group $Fd\bar{3}$, origin at center of symmetry. Positional and isotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esds in the units of the least significant digit given for the corresponding parameter. [b] Occupancy factors are given as the number of atoms or ions per unit cell. [c] The ions at Pd(2) are proposed to be Pd^{4+}; the remaining Pd ions are Pd^{2+}.

the crystal was allowed to cool and was evacuated at room temperature and 2×10^{-6} Torr for 2 h. Care was taken (zeolite beads in series evacuated in situ) to prevent polar molecules from cooler downstream parts of the vacuum system from reaching the crystal. Still under vacuum, it was sealed in its capillary by torch.

The space group $Fd\bar{3}$ was used throughout this work. This choice is supported by (a) the low Si/Al ratio, which in turn requires, at least in the short range, alternation of Si and Al, and (b) the observation that this crystal, like all other crystals from the same batch (unless damaged by harsh chemical treatment), does not have intensity symmetry across (110) and therefore lacks that mirror plane. Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo Kα radiation (Kα₁, $\lambda = 0.709\,30$ Å, Kα₂, $\lambda = 0.713\,59$ Å). The unit cell constant at 21(1) °C determined by least-squares refinement of 25 intense reflections for which $14° < 2\theta < 24°$ is $a = 24.982(4)$ Å.

The $\omega-2\theta$ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 and 0.34° min⁻¹ in ω. The intensities of three reflections in diverse regions of reciprocal space were recorded every 3 h to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reflections in the positive octant of an F-centered unit cell for which $2\theta < 50°$, $l > h$, and $k > h$ were examined by counter methods. Of the 1267 unique reflections examined, only the 196 for which $I > 2\sigma(I)$ were used for subsequent structure determination and refinement, except for the final cycles.

An absorption correction ($\mu = 1.26$ mm⁻¹ and $\rho_{cal} = 1.636$ g/cm³)[12] was made empirically using a ψ scan. The calculated transmission coefficients ranged from 0.982 to 0.989. These corrections had little effect on the final R indices. Other details are the same as previously reported.[13]

Structure Determination

Full-matrix least-squares refinement[14] was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated $Ca_{46}-X$.[13] Initial isotropic refinement of the framework atoms converged to an unweighted R_1 index, $(\sum|F_o - |F_c||)/\sum F_o$, of 0.46 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.40.

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)[a]

Si−O(1)	1.652(16)	O(1)−Si−O(2)	110.4(9)
Si−O(2)	1.589(16)	O(1)−Si−O(3)	107.2(8)
Si−O(3)	1.651(16)	O(1)−Si−O(4)	108.3(9)
Si−O(4)	1.523(19)	O(2)−Si−O(3)	112.3(8)
mean	*1.603*	O(2)−Si−O(4)	102.7(9)
		O(3)−Si−O(4)	115.9(9)
Al−O(1)	1.736(17)	O(1)−Al−O(2)	108.6(8)
Al−O(2)	1.766(16)	O(1)−Al−O(3)	107.3(7)
Al−O(3)	1.708(16)	O(1)−Al−O(4)	113.9(8)
Al−O(4)	1.725(19)	O(2)−Al−O(3)	109.8(7)
mean	*1.734*	O(2)−Al−O(4)	101.1(8)
		O(3)−Al−O(4)	115.9(9)
Pd(1)−O(3)	2.588(13)	Si−O(1)−Al	133.2(9)
Pd(2)−O(3)	2.103(13)	Si−O(2)−Al	140.6(8)
Pd(3)−O(3)	2.371(11)	Si−O(3)−Al	136.1(8)
Pd(4)−O(1)	2.17(5)	Si−O(4)−Al	151.6(9)
Pd(4)−O(4)	2.80(5)		
Na(1)−O(2)	2.258(11)	O(3)−Pd(1)−O(3)	90.8(4)
Pd(2)−O(5)	1.673(3)	O(3)−Pd(2)−O(3)	119.5(5)
Pd(2)−O(6)	2.074(17)	O(3)−Pd(3)−O(3)	99.9(7)
O(5)−O(3)	2.588(13)	O(1)−Pd(4)−O(4)	60.9(14)
O(6)−O(3)	3.061(11)	O(2)−Na(1)−O(2)	115.7(5)
		O(5)−Pd(2)−O(6)	180

[a] Numbers in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding value.

The initial difference-electron-density Fourier function revealed two large peaks at Pd(1) (0.0, 0.0, 0.0) and Na(1) (0.22, 0.22, 0.22) with peak heights of 10.2 and 6.9 e Å⁻³, respectively. Isotropic refinement of the framework atoms, Pd(1), and Na(1) (see Table 2) converged with $R_1 = 0.23$ and $R_2 = 0.24$. A subsequent difference Fourier synthesis showed a peak at Pd(2) (0.04, 0.04, 0.04) with peak height 4.4 e Å⁻³ and another at Pd(3) (0.066, 0.066, 0.066) with peak height 4.0 e Å⁻³. Simultaneous refinement of positional and isotropic thermal parameters for the framework atoms, Pd(1), Pd(2), Pd(3), and Na(1) converged with $R_1 = 0.091$ and $R_2 = 0.082$.

On an ensuing difference Fourier function, two peaks appeared at O(6) (0.08, 0.08, 0.08) with peak height 3.8 e Å⁻³ and Pd(4) (0.421, 0.018, 0.085) with peak height 2.8 e Å⁻³. Simultaneous positional and isotropic thermal parameter refinement with occupancy numbers varying converged with $R_1 = 0.082$ and $R_2 = 0.075$.

The occupancies at site I (Pd(1)) and site I′ (Pd(2)) had refined to 9.6(1) and 16.2(2), respectively. The Pd(2) position appeared to be nicely half full at 16.0. The occupancy at site I (Pd(1)) should then not exceed 8.0 to avoid a too-short Pd(1)−Pd(2)
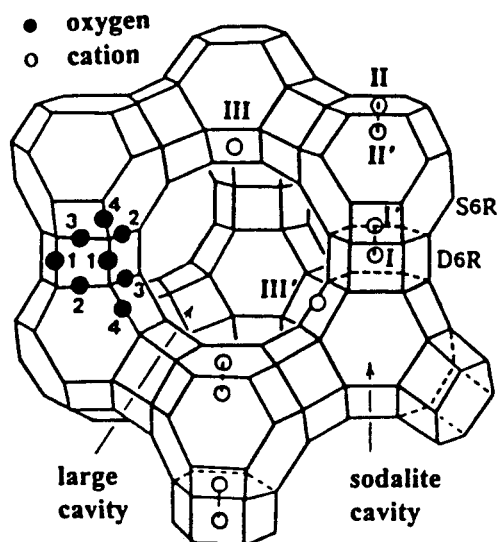
2492 *J. Phys. Chem. B, Vol. 104, No. 11, 2000*

Lee et al.

Figure 1. Framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by numbers 1−4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

intercationic interaction. Also the Pd(1)−O(3) distance, 2.588-(13) Å, is much longer than the sum of the ionic radii of Pd^{2+} and O^{2-}, 0.86 + 1.32 = 2.18 Å. This indicates that oxygens, which have long interaction distances to framework oxygens, may also be present at the Pd(1) position. This position was then assigned to both Pd(1) and O(5). With the occupancy at Pd(1) fixed at 8.0, the occupancy at O(5) refined to 7.7(1) and was fixed at 8.0. Isotropic refinement of the framework atoms, Pd(1), Pd(2), Pd(3), Pd(4), Na(1), O(5), and O(6), converged to $R_1 = 0.069$ and $R_2 = 0.050$ (see Table 1). The occupancy numbers at Pd(1), Pd(2), Pd(3), Pd(4), Na(1), O(5), and O(6) were fixed as shown in Table 1. The final error indices were $R_1 = 0.070$ and $R_2 = 0.051$. The final difference Fourier function was featureless.

The final refinement was done using the 617 reflections for which $I > 0$ to make more use of the diffraction data: $R_1 = 0.306$ and $R_2 = 0.075$. The results are shown in Table 1. This allowed the esds to decrease by about 35% of their former values.

Atomic scattering factors for Si, Al, O^-, Na^+, and Pd^{2+} were used.[15,16] Atomic scattering factors were modified to account for anomalous dispersion.[17] The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2.

Discussion

Zeolite X is a synthetic Al-rich analogue of the naturally occurring mineral faujasite (see Figure 1). The cuboctahedron (14-hedron with 24 vertices) known as the sodalite cavities or β-cages may be viewed as its principal building block. These β cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal prisms) and, concomitantly, to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms but are displaced from those points to give near tetrahedral angles about Si and Al. Single six-rings (S6Rs) are shared by sodalite and supercages
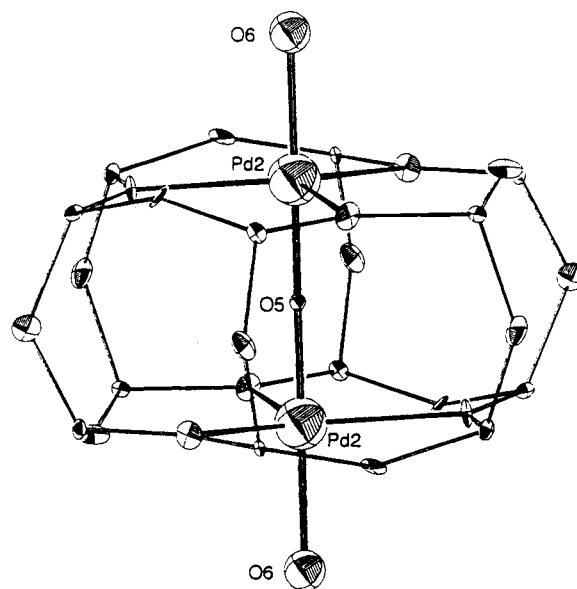

Figure 2. Linear $[HO-Pd^{IV}-O-Pd^{IV}-OH]^{4+}$ cluster found in half of the D6Rs. The terminal hydrogen atoms were not found and are not shown. Ellipsoids of 20% probability are used.

and may be viewed as the entrances to the sodalite cavities. Each unit cell has eight sodalite units, eight supercages, 16 D6Rs, 16 12-rings, and 32 S6Rs.

Exchangeable cations that balance the negative charge of the aluminosilicate framework are found within the zeolite's cavities. They are usually found at the following general sites shown in Figure 1: site I at the center of a D6R, I′ in the sodalite cavity on the opposite side of either of the D6R's six-rings from site I, II′ inside the sodalite cavity near a S6R, II in the supercage adjacent to a S6R, III in the supercage opposite a four-ring between two 12-rings, and III′ somewhat or substantially distant from III but otherwise near the inner walls of the supercage or the edges of 12-rings.

In this crystal structure, palladium ions are found at four crystallographic sites, Na^+ ions are found at one, and nonframework O^{2-} ions are found two.

At the centers of the D6Rs (see Figures 2 and 3), eight Pd^{2+} ions at Pd(1) and eight O^{2-} ions at O(5) fill the 16-fold site-I position. Unfortunately, only the average values for the coordinates at O(3) could be determined in the present work; the small thermal parameter at O(3) indicates that these two positions are not very different. Still the O(3) coordinates in the D6Rs that contain Pd^{2+} ions at Pd(1) should be different from those in the D6Rs that contain O(5) oxide ions. The octahedral Pd(1)−O(3) distance, 2.588(13) Å, is much longer than the sum of the ionic radii of Pd^{2+} and O^{2-}, 0.86 + 1.32 = 2.18 Å,[18] so the O(3)s in Pd(1)-containing D6Rs should be pulled somewhat toward the center. The O(5)−O(3) distance, 2.588(13) Å, is shorter than the sum of the ionic radii of O^{2-} and O^{2-}, 1.32 + 1.32 Å, so the O(3)s in O(5)-containing D6Rs are likely to be pushed outward. The actual Pd(1)−O(3) distance should be shorter than 2.588(13) Å and the O(5)−O(3) distance should be longer. Sixteen palladium ions at site I′ (Pd(2)) are displaced only by a small amount from D6R six-rings into the sodalite cage (see Figures 3 or 4) while the displacement of the two remaining site-I′ ions (at Pd(3)) is much greater (see Figure 4).

Each site I lies betweens two I′ sites (see Figure 1). Sites I (Pd(1)) and I′ (Pd(2)) cannot both be occupied in any given D6R because the resulting intercationic distance would be far too short (1.673(3) Å). Because eight of the 16 D6Rs contain
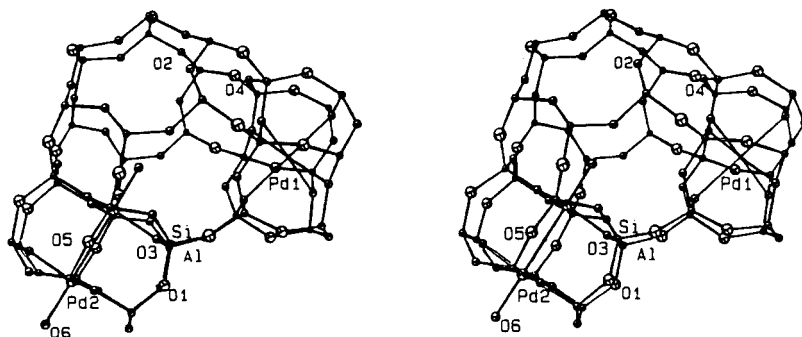
Crystal Structure of Pd^{2+}-Exchanged Zeolite X

J. Phys. Chem. B, Vol. 104, No. 11, 2000 **2493**

Figure 3. Stereoview of a sodalite cavity with two attached D6Rs. One Pd^{2+} ion at Pd(1) (site I), one O^{2-} ion at O(5) (site I), two Pd^{4+} ions at Pd(2) (site I′), and two O^{2-} ions at O(6) (site I′) are shown. Not shown are the remaining two D6Rs that associate with each sodalite cavity; they are similarly occupied. About 75% of the sodalite cavities may have this arrangement (without additional Pd^{2+} ions at Pd(3); those are shown in Figure 4). Ellipsoids of 20% probability are used.
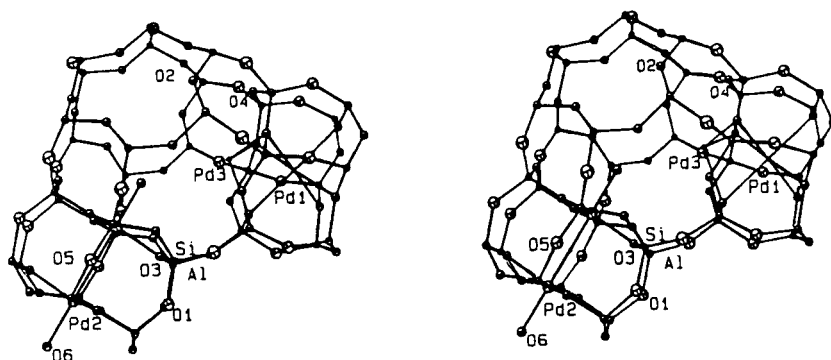

Figure 4. Stereoview of a sodalite cavity with two attached D6Rs. It is the same as Figure 3 except that a Pd^{2+} ion at Pd(3), the sparsely occupied I′ site, is shown. About 25% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are used.
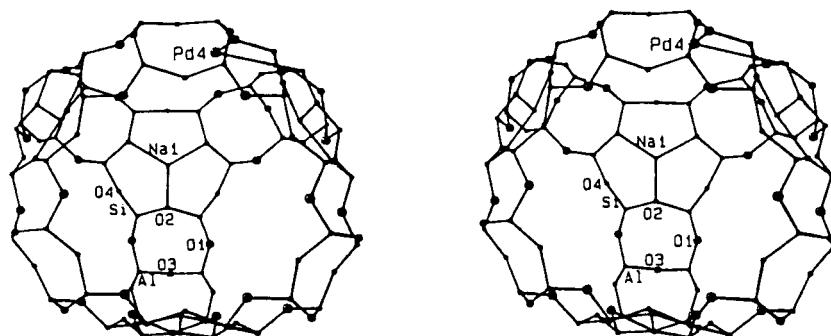

Figure 5. Stereoview of a supercage. Four Na$^+$ ions at Na(1) (site II) and one Pd^{2+} ion at Pd(4) (site III′) are shown. About one in four 12-rings contains a Pd(4) ion. Ellipsoids of 20% probability are used.

a Pd(1) ion, these cannot accommodate any ions at Pd(2). The eight remaining D6Rs must then accommodate all 16 of the ions at Pd(2). Thus, the 16 D6Rs may be considered full with eight Pd(1) ions at site I in half and 16 Pd(2) ions at site I′ in the other half. Each pair of ions at Pd(2) must then be bridged linearly by an oxide ion at O(5).

The Pd(2)−O(3) distance, 2.103(13) Å, is a little less than but comparable to the sum of the ionic radii of Pd^{2+} and O^{2-}, 2.18 Å,[18] as is the Pd(2)−O(6) bond distance, 2.074(17) Å. However the O(5)−Pd(2) bond distance, 1.673(3) Å, is much shorter than that sum, indicating that this Pd ion has been substantially oxidized, perhaps to Pd^{4+}. This is also indicated by the very presence of the nonframework oxide ions at O(5) and O(6) (see Figure 2) and is necessary for charge balance. A 4+ cation requires higher coordination and more anionic ligands, as is seen at Pd(2).

The eight linear O(6)−Pd(2)−O(5)−Pd(2)−O(6) clusters per unit cell are centered in D6Rs and extend into the two adjacent

sodalite cavities (see Figures 2−4). The O(3)−Pd(2)−O(3) bond angle, 119.5(5)° (nearly ideal trigonal planar), indicates that Pd^{4+} fits this six-ring well.

The Pd^{4+}−O^{2-} distances are reasonable. As compared to the sum of the ionic radii of Pd^{4+} and O^{2-}, 0.65 + 1.32 = 1.97 Å,[18] the central ones, Pd(2)−O(5) = 1.673 Å, are too short, and the outer ones, Pd(2)−O(6) = 2.074(17) Å, are too long. This would be expected because the oxygens of the D6R are pulling the Pd(2)s together along the O−Pd−O−Pd−O axis.

The oxidation state of 4+ for the ions at Pd(2) is chosen for reasons other than bond length. It is the only common higher oxidation state for Pd that is likely to result from heating Pd^{2+} in oxygen at 400 °C. Pd^{5+} is another possibility, but this oxidation state is still unknown.[19] Attempts to establish the oxidation state of Pd by measuring the symmetric-stretch frequency by laser-Raman methods at a number of wavelengths were unsuccessful due to high fluorescence. To achieve charge balance, it is proposed that each terminal oxide in the linear cluster

has retained a hydrogen atom, so that the linear cluster is [HO—Pd^{4+}—O^{2-}—Pd^{4+}—OH]$^{4+}$. To maintain an adequate coordination geometry about Pd^{4+}, it is reasonable that this linear cluster would not lose a water molecule at 400 °C. Some La^{3+} ions in overexchanged La^{3+}—X fully dehydrated at 400 °C retain water molecules for the same reason, to maintain an adequate coordination geometry.[20,21]

The ca. two Pd^{2+} ions at Pd(3) occupy another I′ site, in the sodalite cavities opposite D6Rs. Each Pd^{2+} ion lies relatively far inside the sodalite cavity, 1.99 Å from the plane of the three O(3) framework oxygens of the D6R to which it is bound. The Pd(3)—O(3) distance is 2.371(11) Å, much longer than sum of ionic radii, 0.80 + 1.32 = 2.12 Å. The short repulsive approach between Pd(3) and Pd(1), 2.624(13) Å, is likely to be responsible (see Figure 4).

Thirty-two Na$^+$ ions at Na(1) nicely fill the site II position. They are recessed 1.03(1) Å into the supercage from the S6R plane at O(2) (see Figure 5). The Na(1)—O(2) distance is 2.258-(11) Å, comparable to the sum of the corresponding ionic radii, 0.97 + 1.32 = 2.29 Å. Thirty-two is a special number in $Fd\bar{3}$; it suggests that a single site, perhaps I′, remained unexchanged during the ion-exchange process. Ions such as Pd(NH$_3$)$_4^{2+}$ or Pd(NH$_3$)$_4$Cl$^+$ are too large to enter sodalite cavities if they are not sufficiently labile. Perhaps 32 Na$^+$ ions filling site I′ were not replaced during ion exchange.

About four Pd^{2+} ions at Pd(4) lie at site III′ in the supercage (see Figure 5). Each of these Pd^{2+} ions approaches an O(1) oxygen of the zeolite framework most closely. The Pd(4)—O(1) distance is 2.17(5) Å, comparable to the sum of the ionic radii of Pd^{2+} and O^{2-}, 2.12 Å.

The small size of the diffraction data set (only 196 reflections with $I > 2\sigma(I)$) indicates that this crystal has been damaged. H$^+$ ions, introduced either during ion exchange as H$^+$ or NH$_4^+$, or as a result of Pd^{2+} hydrolysis, or as the product of the dissociation of H$_2$Pd$_2$O$_3^{4+}$, are likely to have attacked the zeolite framework to a minor degree at elevated temperatures.

Summary

Thirty Pd cations are found at sites I, I′, another I′, and III′. Sixteen appear to have been oxidized to Pd^{4+} and 14 have remained Pd^{2+}. Eight linear [HO—Pd—O—Pd—OH]$^{4+}$ clusters per unit cell have formed along 3-fold axes. Each cluster extends from one sodalite unit through the center of a D6R into another sodalite unit. The remaining eight D6Rs have Pd^{2+} at their centers. That half of the D6Rs contain O and the other half Pd is an interpretation of the electron density at this position. Site II is full with 32 Na$^+$ ions.

Supporting Information Available: Table of calculated and observed structure factors with esds. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gallezot, P. *Catal. Rev. Sci. Eng.* **1979**, *20*, 121.
(2) Maxwell, I. E. *Adv. Chem. Catal.* **1982**, *31*, 2.
(3) Beer, R.; Calzaferri, G.; Li, J.; Waldeck, B. *Coord. Chem. Rev.* **1991**, *111*, 193.
(4) Herman, R. G.; Lunsford, J. H.; Beyer, H. K.; Jacobs, P. A.; Uytterhoeven, J. B. *J. Phys. Chem.* **1975**, *79*, 2388.
(5) Jacobs, P. A.; Uytterhoeven, J. B.; Beyer, H. K. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 674.
(6) Bergeret, G.; Gallezot, P.; Imelik, B. *J. Phys. Chem.* **1981**, *85*, 411.
(7) Gallezot, P.; Imelik, B. In *Molecular Sieves*; Meier, W. M., Uytterhoeven, J. B., Eds.; American Chemical Society: Washington, DC, 1973; p 66.
(8) Homeyer, S. T.; Sachtler, W. M. H. *J. Catal.* **1989**, *117*, 91.
(9) Homeyer, S. T.; Sachtler, W. M. H. *J. Catal.* **1989**, *118*, 266.
(10) Moller, K.; Bein, T. *J. Phys. C8 (Paris)* **1986**, C8-231.
(11) Bogomolov, V. N.; Petranovskii, V. P. *Zeolites* **1986**, *6*, 418.
(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. II, p 302.
(13) Yeom, Y. H.; Kim, Y.; Song, S. H.; Seff, K. *J. Phys. Chem. B* **1997**, *101*, 6914.
(14) Calculations were performed with Structure Determination Package Programs, MOLEN, Enraf-Nonius, Netherlands, 1990.
(15) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 73.
(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.
(18) *Handbook of Chemistry and Physics,* 70th ed.; The Chemical Rubber Co.: Cleveland, OH, 1989/1990; p F-187.
(19) Lucier, G. M.; Shen, C.; Elder, S. H.; Bartlett, N. *Inorg. Chem.* **1998**, *37*, 3829.
(20) Park, H. S. 1999 M.S. Thesis, University of Hawaii.
(21) Park, H. S.; Seff, K. *J. Phys. Chem. B*, in press.