JOURNAL DE PHYSIQUE

Tome 47 Colloque C8, supplément au n° 12 Décembre 1986

EXAFS and Near Edge Structure IV

July 7-11, 1986
Abbaye Royale de Fontevraud
(France)

Edited by : P. LAGARDE
D. RAOUX
J. PETIAU

Vol. 1

les éditions de physique

Avenue du Hoggar,
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B.P. 112,
91944 Les Ulis Cedex, France

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JOURNAL DE PHYSIQUE
Colloque C8, supplément au n° 12, Tome 47, décembre 1986

EXAFS STUDIES ON THE REDUCTION OF Pd(II) IN X ZEOLITES

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ABSTRACT

Palladium tetraammine ion exchange into zeolite, temperature treatments under different atmospheres, and hydrogen reduction have been studied by EXAFS at the Pd K edge. Complete autoreduction is found to take place between 473 and 623 K under vacuum. A bidisperse Pd metal phase is formed which agglomerates at the expense of the small particles upon prolonged heating at 623 K. In contrast, a similar treatment under oxygen suppresses autoreduction, and the Pd cations remain in zeolite coordination sites. Additional small amounts of palladium oxide are observed under these conditions. If hydrogen is admitted to the dehydrated, ionic system at 295 K, the oxygen coordination of the Pd disappears and evidence is obtained for the formation of Pd(0) dimers that interact with the framework via a long Pd-O bond.

INTRODUCTION

The use of X-ray absorption spectroscopy for the characterization of heterogeneous catalysts became popular in recent years (1). Its sensitivity to short-range order phenomena is particularly helpful if the interaction of molecular complexes or small metal clusters with the support is examined.

The reduction process of Pd, ion exchanged into zeolites, has been studied by using XRD (2,3), TPD/MS (4), XPS and ESR techniques (5,6). Pd^{2+} ions are found to undergo autoreduction if ammine ligands are present in the zeolite pores (4). Particle sizes of a few nm have been stabilized in the zeolite matrix, and low temperature hydrogen reduction was reported to render "atomically disperse" Pd (2,3) and Pd(I) species (6).

The present study is aimed at a more detailed understanding of the Pd reduction process in the zeolite environment. EXAFS complements the use of XRD for this system since it detects metastable species lacking long range order.

EXPERIMENTAL

The Pd zeolites were obtained by ion exchange with an 0.018 m aqueous solution of $Pd(NH_3)_4Cl_2\ H_2O$ (Alfa #88878) into zeolite X (Alfa 13 X, #020684; Si/Al=1.2) at RT for 16 hours, excessive washing until chlorine free and drying at 300 K, yielding a unit cell composition of $Na_{46}Pd_{20.5}(AlO_2)_{87}(SiO_2)_{105}\ 235\ H_2O$.

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Temperature programs were run at a linear heating rate of 2 K/min. All temperature treated samples were kept at 363 K for at least 10 hours.

Vacuum treatment was performed under dynamic conditions under less than 10-4 torr. 600 torr of hydrogen was admitted at RT for 1 hour, whereas reduction at elevated temperatures as well as argon or oxygen treatments were done under a gas stream in tube reactors. All samples were evacuated after heat treatment until cooled down to RT. Gases were purified by water or oxygen absorbing traps.

Zeolite samples were embedded in a mixture of octadecane, dodecane 1:1 at 310 K under exclusion of oxygen and moisture in a glovebox to give a total X-ray absorption of less than 2 and edge steps close to 1. Wafers were kept under nitrogen until measured at the synchroton. A 1.8 m solution of $Pd(NH_3)_4Cl_2$, PdO powder and a 0.025 mm Pd foil were used as references.

X-ray absorption measurements were conducted at the X-11A beamline at NSLS in December 1985 and May 1986 with an electron energy of 2.5 GeV and ring currents between 40 and 120 mA. Data were collected with a Si(400) crystal pair at the Pd K edge (24 keV) at ca. 100 K.

Data analysis was performed with the University of Washington package. The photoelectron energy origin E_0 was chosen to be at the inflection point of the edges. Normalization, background removal, Fourier transformation (FT) and Fourier filtering (FF) of unknown and references were done over similar ranges to allow a direct comparison between several data sets. FT of files showing mainly the ammine complex were done between 2.6 and 12.8 k and those of the metal containing samples between 2.6 and 17.5 k. The magnitudes of the FT are compared without phase shift correction.

Electron micrographs were taken on a HITACHI H600 from microtomed sections of 80 to 90 nm thickness. Samples were embedded in EPON 812 under exclusion of air.

RESULTS AND DISCUSSION

A) Ion exchanged PdX zeolites

The FT of the Pd2+ tetraammine complex in solution as well as in crystalline form show a major contribution at 1.61 A caused by the four planar coordinated ammine ligands and additional water molecules (Fig 1). Following the literature (7), the real Pd-N distance is set to 2.06 A. The higher shell scattering is proposed to be due to the chloride counter ion as is indicated by its dependence on different weighing schemes.

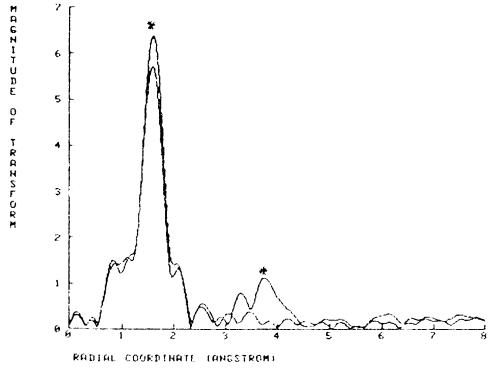

Figure 1 k^3 weighed FT of(*)1.8 m solution of $Pd(NH_3)_4Cl_2$ reference and exchanged into zeolite X

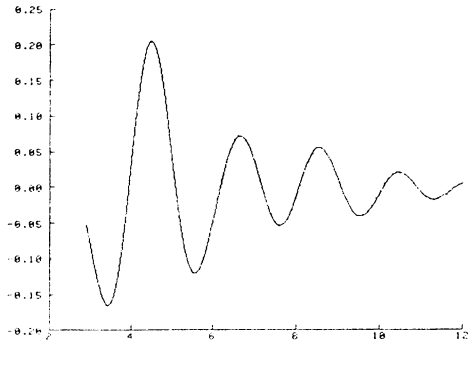

Figure 2 k^1 weighed FF (-) 0.31 to 2.6 A and fit (..) of $Pd(NH_3)_4$ exchanged zeolite

Comparison with the FT of the ammine complex exchanged into the framework of NaX zeolite (Fig. 1) shows strong similarities. Backscattering of the chloride is vanished, and the absence of outer shell scattering indicates that the $[Pd(NH_3)_4]^{2+}$ ion does not occupy preferred coordination sites at the negatively charged framework of the zeolite. A fit of the k1 weighed CHI-function, backtransformed between 0.31 and 2.6 A, gave an excellent agreement with the reference with N=6.53, R=2.055 A, ΔE_0=1 eV and SIG^2=0.0009 A^2(Fig.2).

These results suggest that the identity of the complex is maintained upon ion exchange and that it is randomly oriented in the zeolite supercages. Similar observations were reported for Ni (8), Co or Mn cation exchange into NaY zeolite (9,10).

b) Vacuum treatment

Pd samples were treated under vacuum at 363 K for 10 hours, at 473 K for 1 hour and at 623 K for 1 and 10 hours. As shown in a TPD/MS study of the decomposition process (4) of the zeolite supported ammine complex, evolution of NH_3 occurs in two steps at 320-360 K and 420-470 K. The EXAFS data of the samples taken at 363 and 473 K are strikingly similar to those of the starting material. Even at 473 K there is only a slight decrease in magnitude of the main peak. The magnitudes of the FT in Fig. 3 demonstrate that a small new peak arises at 473 K, supposedly from a different bonding to the zeolite framework.

This is strongly supported by the fitting results: only the sample at 363 K gave a reasonable result with N=6.00, R=2.069 A, ΔE_0=0 eV, and SIG^2=0.0008 A^2. In contrast, an additional contribution at 473 K made it impossible to fit this sample with the precursor alone.

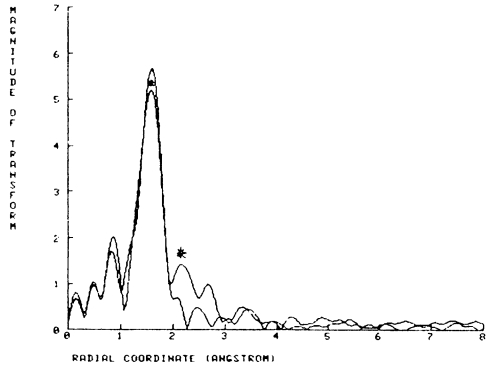

Figure 3 k^3 weighed FT of 363 K and 473 K (*) vacuum treated $Pd(NH_3)_4$ zeolite

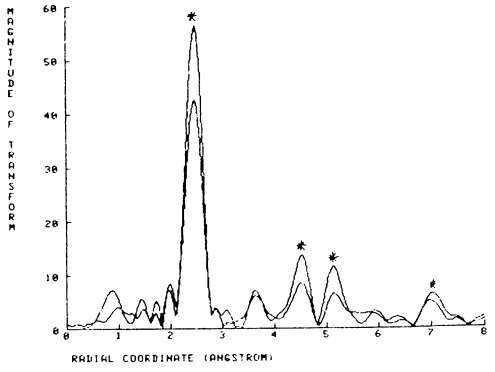

Figure 4 k^3 weighed FT of 623 K vacuum treated $Pd(NH_3)_4$ zeolite after 1 and 10 (*) hours

Since ammonia evolution must have taken place at this step, we explain the sixfold coordination with a replacement of complex ammine ligands by oxygen of the six-membered rings of the zeolite. Nitrogen and oxygen can not easily be distinguished with EXAFS, because both backscattering amplitude and phase shift of these elements are nearly identical. We assume that up to 473 K, two or three ammine ligands remain at the Pd ion in addition to the zeolite oxygen coordination.

Heating the sample up to 623 K causes dramatic changes in the EXAFS. Fig. 4 shows the formation of Pd metal already after 1 hour at this temperature, with bulk-like shells and the total disappearance of the ionic

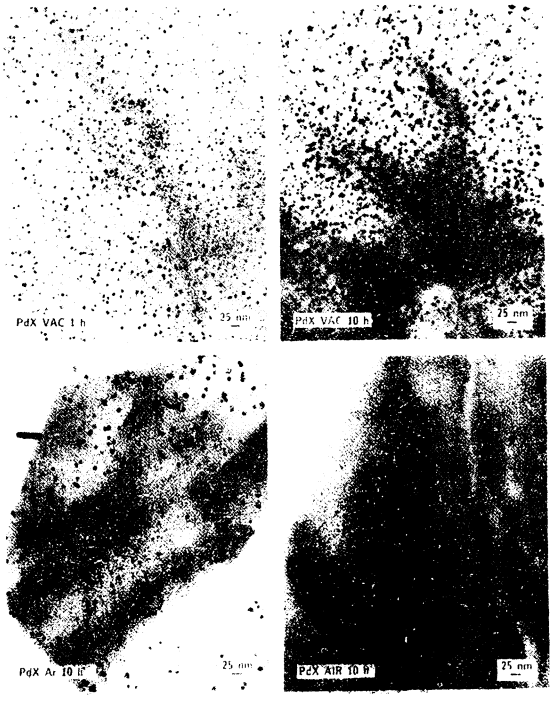

Figure 5 electron micrographs of $Pd(NH_3)_4$ zeolite after 1 and 10 hour vacuum, 10 hour argon and 10 hour air treatment at a magnification of 300 000

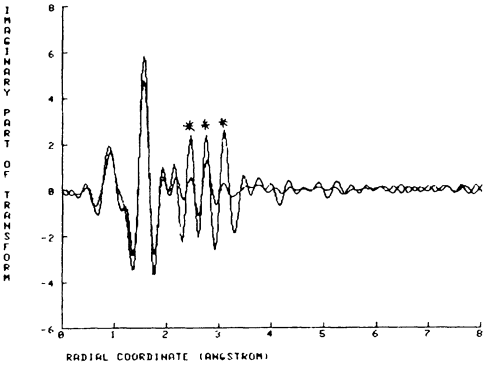

Figure 6 k^3 weighed FT of 523 K and 623 K (*) air treated $Pd(NH_3)_4$ zeolites

Pd-OZ(zeolite) bond. The magnitude of all shells increases at prolonged heating. A fit of the first shell with Pd foil as reference gives N=7, R=2.73 A, ΔE_0=0 and SIG^2 = 0.0001 A^2.

The average coordination number of N = 7 suggests an average particle size of about 1 nm, whereas the outershell scattering indicates significant contributions of larger particles. This requires the presence of a bidisperse system with one -undetected- fraction showing very low Pd-Pd coordination numbers or unreduced Pd^{n+} ions, and another fraction of bulk-like particles. These larger particles (2-3 and 7-9 nm) are observed in the corresponding electron micrographs (Figure 5 top left). They agglomerate to a size of 7-9 nm upon prolonged heating (Figure 5 top right.) It is striking that all particles remain occluded in the zeolite matrix even when exceeding the supercage dimensions of 1.3 nm. Both findings are supported by XRD and XPS measurements (11).

Subsequent hydrogen treatment at 323 and 423 K shows that the samples are stable against further sintering. A similar procedure under argon atmosphere results in particles of 9-12 nm diameter (Fig. 5 bottom left).

These EXAFS results complete the earlier proposed picture of an autoreduction process of $Pd(NH_3)_4$ in zeolites: it is clear now that ammonia liberation and reduction are two distinct steps. The autoreduction is caused by the remaining 1 to 2 ammine ligands.

C) Decomposition in air

If $Pd(NH_3)_4$ zeolites are heated in air or oxygen up to 523 K, the corresponding EXAFS data resemble those obtained from the vacuum treatments. In contrast, further heating in air to 623 K does not produce Pd metal as observed under vacuum (Fig. 6). The Pd cations still occupy lattice oxygen sites , showing that the autoreduction is completely suppressed in air. A minor fraction of larger PdO particles of ca. 15% is indicated in the

imaginary part of the FT by Pd-O-Pd features like in the PdO reference. No significant differences are observed if pure oxygen is used. Electron micrographs confirm the EXAFS results and show a minor amount of particles with a size of 2-3 nm (Fig. 5 bottom right).

The most interesting result is achieved when exposing this sample to 600 torr of hydrogen at 295°K. A color change from orange brown to brown appears within the first minutes. The FT of this sample shows that a complete reduction occured already under these mild conditions (Figure 7). Only one single shell is observed representing Pd-Pd scattering. No oxygen scattering with the Pd-O distance of 2.07 Å typical for Pd^{2+} sites in zeolite framework coordination (Figure 6) can be detected after admission of hydrogen. This can only be understood in terms of a complete removal of the Pd from this coordination environment upon reduction.

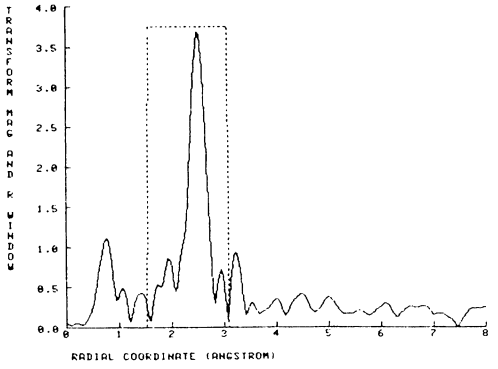

Figure 7 k^3 weighed FT of 623 K air and subsequent 295 K H_2 treated $Pd(NH_3)_4$ zeolite

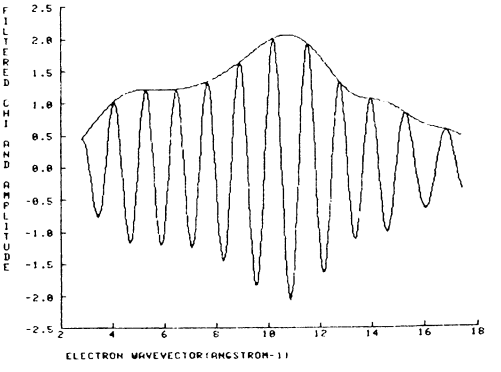

Figure 8 k^3 weighed sample from Fig. 7 FF over the indicated window

An attempt to fit this system with Pd foil as reference yields a maximum number of 1.5 neighbor atoms and a bond length similar to bulk metal. The FF envelope of this peak (Fig. 8) also detects an additional contribution of another low Z scatterer, presumably oxygen. This interaction is believed to be due to a Pd-O bond with zeolite oxygen, which overlaps with the Pd-Pd peak in the FT (Figure 7) and is significantly longer than the ionic Pd^{2+}-OZ bond. A determination of this Pd-O bond distance is the subject of further studies. Comparable results with long bonds between metal clusters and oxygen of oxide supports were recently obtained for Rh (12) and Os (13).

XRD results of comparable experiments with a Pd-zeolite system had been interpreted in terms of atomically dispersed Pd(0) which was undetectable by this technique (2,3). XPS and ESR literature related to this work shows the difficulty of band assignment to different Pd species. XPS bond energies which differ by 0.1 eV were either referred to PdO, atomically dispersed Pd(0) (5), or to Pd(I) and charged clusters (6).

We believe to have evidence for the formation of extremely small Pd(0) clusters - most likely dimers - that show weak interaction with zeolite framework oxygen.

The authors would like to thank Steve Heald, John Tranquada, Jack Scrofani and Larry Fereria for assistance during data collection, Michael Van Kavelaar for preparing electron micrographs and the "Deutsche Forschungsgemeinschaft" for financial support. Part of this work was supported by DOE grant # DE-AS0580ER10742.

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