# FORMATION OF REACTIVE CLUSTERS IN Pd-Y ZEOLITE BY REDUCTION-REOXIDATION TREATMENT*

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Received September 13, 1991
Accepted October 22, 1991

Preparation of a finely dispersed Pd-Y zeolite has been investigated by temperature-programmed reduction (TPR) and extended X-ray absorption fine structure (EXAFS) techniques. Upon the treatment by a sequence of calcination, reduction, and reoxidation, the original $Pd(NH_3)_4^{2+}$ ions in the zeolite transformed to reactive species, which were reduced with hydrogen at room temperature and characterized as small PdO clusters of about 25 Pd atoms.

During the last decade considerable research efforts in the field of catalytic science have been directed toward preparation and characterization of highly dispersed metal catalysts. Zeolites, with high ion exchange capabilities and well-defined pore structure, are considered to be excellent supports for these catalysts. On zeolites, active species tend to be more homogeneous in size and shape due to geometric constraints of the lattice. The catalytic activities of metal-exchanged zeolites depend markedly on the prior treatments, which govern the quality and quantity of their catalytic centers.

We have recently investigated the catalytic behavior of Cu-Y zeolite activated by a preliminary treatment. An active copper species was formed by a sequence of calcination, reduction and reoxidation treatments, and identified as small CuO clusters in the lattice[1]. Upon reduction, the clusters were directly reduced to Cu metal at a considerably low temperature[2], while the original $Cu^{2+}$ ions in Y-zeolite were reduced by a two-step mechanism, via $Cu^{+}$ ions to Cu metal, at higher temperatures[3]. The catalytic activity of the activated zeolite in CO oxidation, increased proportionally with the amount of these clusters[4], which could function as catalytic centers via the reversible redox mechanism[5].

In the present work, the availability of the consecutive reduction–reoxidation (R–O) treatment was examined for the formation of active species in palladium–zeolite system. The R–O treatment consists of three stages, i.e., preliminary calcinat-

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* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8 — 13, 1991.*

ion, reduction with hydrogen and reoxidation with oxygen. Palladium ions are, in most cases, introduced into zeolites by exchange with tetraamine salts. Calcination for amine removal of these ions in inert gases or under vacuum results in the formation of large metal particles due to autoreduction and migration of metallic species[6], but treatment in an oxygen stream can yield well dispersed catalyst. Sachtler and co-workers[7-9] have extensively studied the effects of calcination on the location, ligancy and reducibility of metal cations in the zeolite matrix and revealed important roles of preliminary calcination in preparation of highly dispersed Pd-Y zeolite.

Among the techniques for the investigation of active species in zeolites the temperature-programmed reduction (TPR) is found to be the simplest method[10,11]. In the studies of metallic components in zeolites, particles are so small as to escape conventional measurements, such as X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). The extended X-ray absorption fine structure spectroscopy (EXAFS) is well suited to this purpose since it can pursue changes of local structure around metal atoms[5,12,13]. From these points of view, the formation process and structure of the active species in Pd-Y with R–O treatment were investigated by means of TPR and EXAFS techniques, respectively, in the present report.

## EXPERIMENTAL

The Pd-Y zeolite (7 wt. % Pd) was prepared by the conventional method from Linde LZY-52 molecular sieve using $Pd(NH_3)_4Cl_2$ solution. The ion exchange was carried out overnight and the sample was then washed, dried, pelletized, sieved and stored over a saturated ammonium chloride solution.

TPR measurement was performed by a conventional circulation system[2]. A small aliquot (600 mg) of the sample was cooled to 200 K under vacuum, then the temperature of the bed was increased under 10 kPa of the initial hydrogen pressure up to 750 K at 5 K $min^{-1}$. The hydrogen consumption during the TPR process was estimated from the pressure decrease measured by a computer-interfaced pressure transducer (MKS 222B).

Temperature-programmed mass spectrometry (TPMS) measured in a flow system consisted of a gas-feeding manifold with mass-flow controllers and a quartz reactor in an infrared image furnace. A pressure-reducing system combined with a computer-interfaced mass spectrometer (ULVAC MSQ-150A) downstream of the catalyst enabled continuous product analysis of a variety of mass numbers.

Activation of Pd-Y zeolite was performed by the R–O treatment which consisted of three stages, i.e., calcination, reduction, and reoxidation. The calcination was carefully carried out at various temperatures for 60 min under atmospheric pressure of oxygen in order to prevent autoreduction of palladium ions and agglomeration of reduced metal. The reduction and reoxidation of the calcined sample were carried out in the circulation system with hydrogen and oxygen, respectively, under the initial pressure of 10 kPa for 30 min at desired temperatures.

Details of the EXAFS instrument employed were described elsewhere[14]. Basically, it consists of a rotating anode X-ray generator (Rigaku RU-300), a spectrometer with bent Ge(660) and LiF(200) crystals of Johanson cut, ion chambers, slits and counting electronics, which are connected by a computer through a CAMAC bus. The X-ray source with a gold target was operated at 50 kV and 280 mA. The Pd-Y sample was pressed into thin wafers and treated similarly to the TPR experiments in an in situ sample chamber prior to measurements at room temperature.

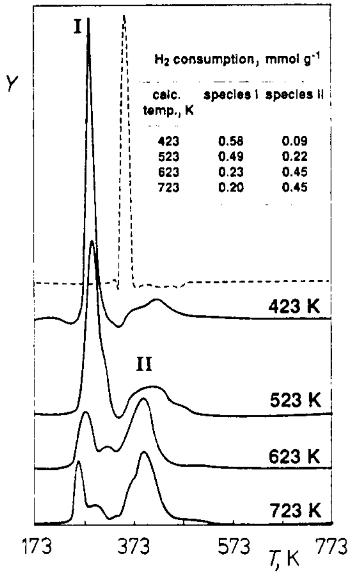
## RESULTS AND DISCUSSION

### *Formation of Active Species*

The original $Pd(NH_3)_4^{2+}$ ions in the zeolite lattice were reduced with hydrogen at 360 K, as shown by the dotted curve in Fig. 1. Only one sharp peak appears in the TPR spectrum, indicating that most of bulky $Pd(NH_3)_4^{2+}$ ions are located in the supercages[7-9]. The broad negative peak around 450 K is presumably due to untrapped hydrogen and nitrogen formed by the decomposition of amine ligands.

Profiles of TPR spectra for Pd-Y after the R–O treatment are depicted by the solid curves in Fig. 1. After activation by the R–O treatment, the spectra consist of two peaks, I and II, with maxima around 280 and 390 K, respectively. The peak at 360 K for the original sample disappears completely from these spectra, suggesting that $Pd(NH_3)_4^{2+}$ ions transform to species I and II corresponding to the peaks I and II, respectively, during the R–O treatment.

The formation of these species depends on the condition of each stage in the R–O treatment, such as calcination, reduction, and reoxidation. In order to evaluate the effect of three stages on the formation of species I and II, the amounts were



H₂ consumption, mmol g⁻¹

| calc. temp., K | species I | species II |
|---|---|---|
| 423 | 0.58 | 0.09 |
| 523 | 0.49 | 0.22 |
| 623 | 0.23 | 0.45 |
| 723 | 0.20 | 0.45 |

FIG. 1

TPR profiles of Pd-Y before (broken curve) and after (solid curves) the R-O treatment at temperatures given at the curves. *Y* rate of $H_2$ consumption in arbitrary units estimated from the area of each peak in the TPR spectra measured under various conditions. The total amounts of hydrogen consumption in the TPR process up to 750 K was substantially independent of the conditions in the R–O treatment and almost corresponded to the amount needed for the complete reduction of palladium ions present in the original sample, i.e., two hydrogen atoms were consumed per one cation and no appreciable adsorption of hydrogen took place during the TPR process.

Among the three stages in the R–O treatment, the first calcination stage shows the most significant influence for the formation of reactive species I. With the rise in calcination temperature under common conditions in the subsequent reduction and reoxidation stages, the amount of species I markedly decreases, whereas that of species II increases, as shown in Fig. 1. This can be attributed to the location of palladium ions in the zeolite lattice. $Pd(NH_3)_4^{2+}$ ions are initially exchanged into the supercages, where the subsequent reduction and reoxidation easily take place. At higher calcination temperatures, the tetraamine ions are stepwise destroyed and swiftly migrate into smaller cages[7]. From this point of view, the peak II found at a high temperature probably corresponds to the reduction of ligand-free $Pd^{2+}$ ions in the sodalite cages[9] with strong electrostatic field.

The stepwise decomposition of amine ligands during the calcination in an oxygen stream is roughly demonstrated in the TPMS profile, as shown in Fig. 2. The ammo-

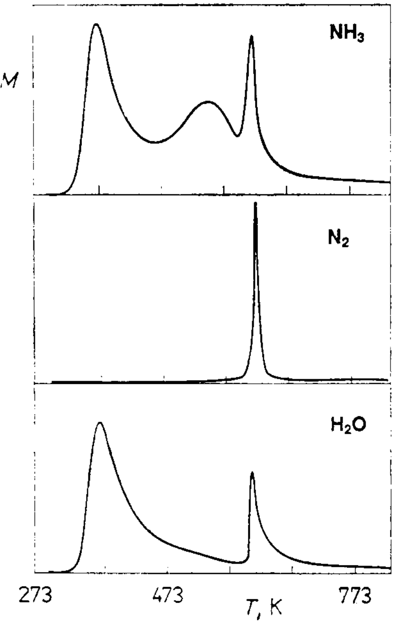


FIG. 2

TPMS profiles of ammonia, nitrogen and water from Pd-Y during calcination in oxygen stream. *M* respons: in arbitrary units nia spectrum consists of three peaks with maxima at 380, 540, and 610 K, which are presumably attributed to the formation of $Pd(NH_3)_2^{2+}$ ions in the supercages, $Pd(NH_3)^{2+}$ and $Pd^{2+}$ ions in the sodalite cages[7], respectively. Only the final decomposition is found to be accompanied by evolution of nitrogen and water. The process of stepwise decomposition is qualitatively substantiated by color changes of the sample after calcination at various temperatures[7], i.e., the original white sample turns yellow and then pink with increasing calcination temperature.

The conditions in the reduction and reoxidation stages of the R–O treatment, on the other hand, show less remarkable effects on the formation of species I in comparison with that of the calcination. In the temperature range from 423 to 723 K, the formation of species I slightly increases with the increase in reduction temperature and with the decrease in reoxidation temperature. It is speculated, thus, that at a low calcination temperature of 423 K, most of palladium ions remain in the supercages as $Pd(NH_3)_2^{2+}$ ions, which transform to species I upon reduction followed by reoxidation. At higher calcination temperatures above 470 K, some portions of the original ions probably migrate into small cages and reoxidize back to $Pd^{2+}$ ions due to the higher electronic stabilization and higher coordination to the lattice oxygen ions. In summary, optimum temperatures for the R–O treatment of Pd-Y are found to be 423, 773, and 673 K, respectively, in the calcination, reduction, and reoxidation stages.

### *Structure of Active Species*

In order to investigate the chemical structure of active species formed in the Pd-Y zeolite, EXAFS spectra were measured after each stage in the R–O treatment. Representative observed spectra $\ln(I_0/I)$ and the normalized EXAFS functions $\chi(k)$ are illustrated in Fig. 3, where $I$ and $I_0$ are count numbers with and without the sample, respectively. In the analysis of EXAFS spectra, the oscillatory part was subtracted, then converted to $k$ space and Fourier transformed into real space by the single scattering theory[15], as follows:

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} \exp\left[-2(\sigma_j^2 k^2 + R_j/\lambda)\right] F_j(\pi, k) \sin\left(2kR_j + \alpha_j(k)\right), \qquad (1)$$

where $k$ is the photoelectron wave vector, $R_j$ is the distance from Pd atoms to atoms in the $j$-th shell, $N$ is the coordination number of Pd atoms, $F$ is the scattering amplitude, $\sigma$ is the Debye–Waller factor and $\alpha$ is the phase shift. The EXAFS function, $\chi(k)$, was then transformed by weighting $k^3$ to yield the radial distribution function $\Phi(R)$, as follows:

$$\Phi(R) = \sqrt{\tfrac{1}{2}} \int k^3 \chi(k) \exp\left(-2\pi kR\right) \mathrm{d}k\,. \qquad (2)$$

The radial distribution functions for Pd-Y after various treatments are shown in Fig. 4. The least-squares curve fitting with the back-transformed oscillation in $k$ space was, furthermore, performed by the use of Eq. (*1*). The "best-fit" values of structural parameters obtained by these curve fittings are summarized in Table I together with those of reference materials.

In the radial distribution function of the original sample a predominant peak is observed at $R$ = 2·08 Å, which probably corresponds to an average distance of the Pd—N bond between $Pd^{2+}$ ions and amine ligands and the Pd—O bond between $Pd^{2+}$ ions and lattice oxygen ions in the supercages. The exact distances of these two bonds have not been determined separately. Upon calcination of Pd-Y at 523 K, these bonds shrink slightly and the coordination number decreases from 5·9 to 3·4, indicating the partial decomposition of amine ligands. Since the reduced

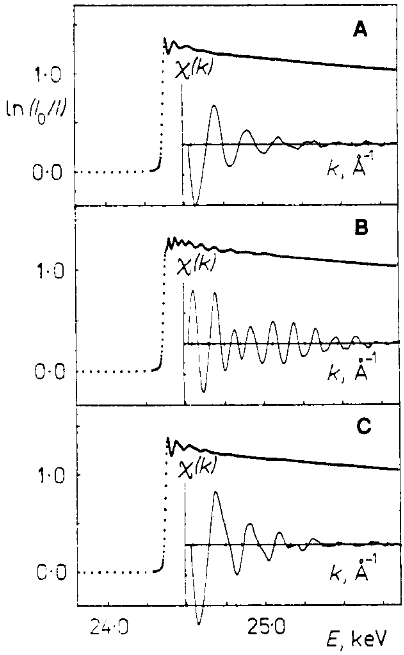


FIG. 3

Normalized spectra and extracted oscillations of EXAFS for Pd-Y after A calcination at 523 K, B reduction at 673 K and C reoxidation at 673 K during the R–O treatment

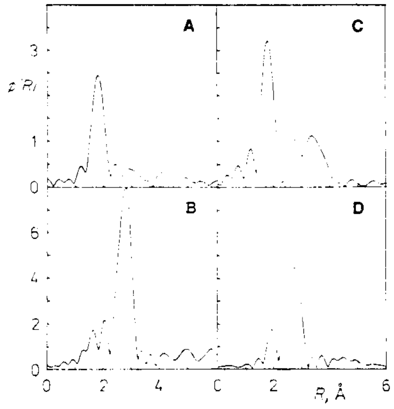


FIG. 4

Fourier transforms of $k^3\chi(k)$ functions for Pd—Y after A calcination at 523 K, B reduction at 673 K, C reoxidation at 673 K, and D reduction at 323 K, where each peak is slightly displaced from true distance because of the phase shift sample shows the characteristic oscillation of metal in the EXAFS function (Fig. 3B) and the Pd—Pd distance of $R$ = 2·75 Å in the $\Phi(R)$ function (Fig. 4B), palladium ions are reduced to metal almost completely at 673 K in the reduction stage.

TABLE I

Best-fit values of structural parameters of Pd-Y from EXAFS data in sequence with each stage in the R–O treatment

| Sequence | Sample treatment | Bond | $R$, Å | $N$ |
|---|---|---|---|---|
| 1 | original Pd-Y | Pd—N(O) | 2·08[a] | 5·9[a] |
| 2 | calcined at 523 K | Pd—O(N) | 2·04[b] | 3·4[b] |
| 3 | reduced at 673 K | Pd—Pd | 2·75 | 9·6 |
| 4 | oxidized at 673 K | Pd—O | 2·04 | 4·5 |
| 5 | reduced at 323 K | Pd—Pd | 2·75 | 6·8 |
| — | Pd foil | Pd—Pd | 2·75 | 12·0 |
| — | PdO powder | Pd—O | 2·03 | 4·0 |

These values are simulated from [a] Pd—N and [b] Pd—O scatterings.

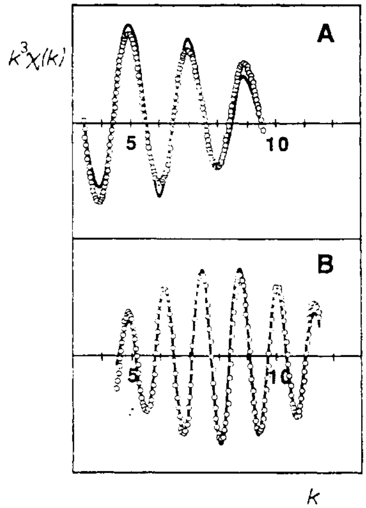


FIG. 5

Comparison of inverse Fourier transforms (solid curve) with calculated values (circles) for A Pd-Y with the R–O treatment and B the sample after reduction of A

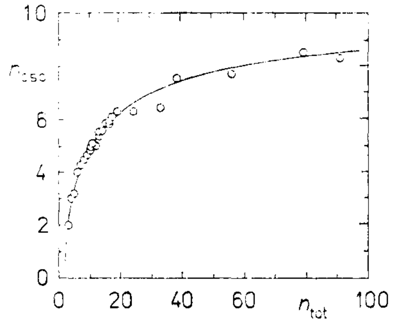


FIG. 6

The plot of average number of osculating atoms ($n_{osc}$) versus number of Pd atoms in the clusters ($n_{tot}$)

After the subsequent reoxidation of the reduced sample, the main peak in Fourier transform appears at $R = 2{\cdot}04$ Å as shown in Fig. 4C. This agrees well with the Pd—O distance in PdO powder ($R = 2{\cdot}03$ Å), although no significant difference is observed in comparison with that in the original sample ($R = 2{\cdot}08$ Å). As illustrated in Fig. 5A, furthermore, inverse Fourier transforms of this peak (solid curve) well reproduces the calculated $k^3\chi(k)$ (circles) from the Pd—O scattering in PdO crystal.

When Pd-Y with the R-O treatment is reduced at a low temperature of 323 K, where peak I is observed in the TPR spectrum, a distinct peak appears at $R = 2{\cdot}75$ Å in the radial distribution function, as shown in Fig. 4D. This value coincides with the Pd—Pd distance in Pd foil. Inverse Fourier transform of this peak (solid curve) reproduces completely the calculated values (circles) from the Pd—Pd scattering in Pd metal, as demonstrated in Fig. 5B. It clearly shows the dramatic effect of the R-O treatment, since the original palladium ions in Pd-Y is reduced at a much higher temperature of 360 K.

The coordination number in the metal formed from species I ($N = 6{\cdot}8$) is extremely smaller than that in infinite crystals ($N = 12{\cdot}0$). The discrepancy between these values is attributed mainly to the difference in the particle size of metal, i.e., the coordination number in small particles is smaller than that in large crystals because of the high proportion of surface atoms. The average size of metal particles formed upon reduction of the species I is calculated from the coordination number, as follows. First, the model of Pd clusters consisting of various numbers of spherical atoms is drawn by computer according to the close-packed structure. Then, the number of atoms in contact with a given atom is counted. Such countings are carried out for all atoms in various sizes of clusters. The average number of osculating atoms will give the average coordination number in the given size of clusters. The results are shown in Fig. 6. The Pd clusters with $N = 6{\cdot}8$, thus consist of 25 atoms. Taking the interatomic distance of $2{\cdot}75$ Å into consideration, furthermore, the average diameter of these clusters is estimated to be $9 - 11$ Å. This size of clusters almost corresponds to the main cavity size of faujasite framework (ca 12 Å) and is so small as to escape conventional XRD or TEM observation. From the points of view so far described, it is plausible that species I corresponds to small PdO clusters in the supercages and the species II are $Pd^{2+}$ ions in the sodalite cages of Y-zeolite.

*We express our gratitude to Professor Y. Udagawa, Dr K. Tohji (Tohoku University, Sendai, Japan) and Dr T. Mizushima (Toyohashi University of Technology, Toyohashi, Japan) for their valuable supports in EXAFS experiments. This work was partially supported by a Grant-in-Aid for Scientific Research (03650657) from the Ministry of Education, Science and Culture of Japan.*

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