

Electron Spin Echo Modulation Studies of the Hydration of Paramagnetic Rhodium Centers in Rh-Y-Zeolite

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A Rh(II) species previously formed in Y-zeolites by heating in flowing oxygen followed by exposure to oxygen and water has been examined by electron spin echo modulation spectrometry to determine the water coordination. Three-pulse electron spin echo experiments on samples exposed to D₂O indicate interaction of Rh(II) with four deuterons at a distance of 0.29 nm with a 0.1-MHz isotropic coupling. This suggests interaction with two water molecules or with one water molecule plus two hydroxyl groups in the first coordination sphere. Aluminum modulation from the zeolite lattice is also observed and indicates that the Rh(II) is most probably in the sodalite cage.

INTRODUCTION

Rhodium catalysts have been the subject of numerous investigations since they have been found to be extremely active in reactions from hydrogenation to induction of polymerization (1-6). In most of these studies it was concluded that the behavior of rhodium catalysts was very much dependent on the degree of dispersion, chemical nature, and oxidation state of rhodium in the catalyst. Although several infrared spectral investigations of rhodium complexes have been reported (7-10) the oxidation state of rhodium and its immediate coordination sphere remains somewhat ambiguous.

On the basis of ESCA results Kuznicki and Eyring (11) suggested that metallic rhodium produced by activation of Rh(III)-exchanged Y-zeolite is responsible for the catalytic activity. Several electron spin resonance (ESR) studies have also appeared on the nature of rhodium in rhodium-exchanged Y-zeolites. Atanasova *et al.* (12) suggested that pairs of Rh ions, e.g., Rh¹⁺-Rh⁰ or Rh²⁺-Rh¹⁺ form in the zeolite super cages and agglomerate on adsorption of water. In contrast to this Naccache *et al.* (13) suggested the formation of

Rh-peroxo species, Rh(II)-O-O-Rh(II), in the sodalite cages of the zeolite which changes into some hydrated Rh(II) monomer species on adsorption of water. They also suggested that hydration in the presence of oxygen may even oxidize Rh(I) to paramagnetic Rh(II). It is important to characterize the hydrated rhodium species as it is known to have a key role in the carbonylation of alcohols over rhodium-exchanged zeolites (14). Recently we have shown (15-18) that analysis of electron spin echo modulation (ESEM) can provide information on the immediate environment of a paramagnetic species. In this paper we report the results of such an analysis carried out for Rh-NaY/D₂O systems and show that the hydrated species is most probably coordinated to two water molecules, or to one water and two hydroxyl groups, near a six-ring in the zeolite structure.

EXPERIMENTAL

Rhodium-exchanged Y-zeolite (Linde SK-40) was obtained by the method of Naccache *et al.* (13). Samples of 0.34, 0.57, 1.0, 3.1, and 6.0 wt% Rh were prepared. Assuming complete exchange the number of rhodiums per unit cell are 0.51, 0.96, 1.7,

5.3, and 10.4, respectively. The ESE results were the same in all the samples except for the 6 wt% Rh. In that sample the phase memory time in the ESE experiments was too short to allow qualitative analysis of the modulation. The use of NH_4Y instead of NaY as the starting zeolite resulted in slightly longer echo decay times. The zeolite samples were heated in flowing oxygen while the temperature was raised slowly to 770 K. After evacuating the samples to a residual pressure of 10^{-5} Torr at the same temperature, they were cooled to ambient temperature and then exposed to 90 Torr O_2 for 10–15 min and then to 23 Torr H_2O or D_2O vapor for 10–15 min. Similar results were obtained for simultaneous exposure to O_2 and H_2O . The exposure times were varied to get the appropriate ESR spectra. Then the samples were transferred *in vacuo* into 3-mm o.d. Suprasil quartz tubes and sealed.

ESR spectra were obtained on a Varian E-4 spectrometer at 77 K and the electron spin echo spectra were recorded with a home-built spectrometer (18) at 4.2 K.

RESULTS AND DISCUSSION

Figure 1 shows the ESR spectrum of activated Rh–NaY zeolite exposed to O_2 and H_2O . It is identical to that reported by Nac-

cache *et al.* (13) and to that of its deuterated analog. The five line structure reported by Atanasova *et al.* (12) was not observed in any of our samples and thus we conclude that multivalent rhodium pairs such as $\text{Rh}^{1+}\text{--Rh}^0$ or $\text{Rh}^{2+}\text{--Rh}^{1+}$ are absent in our samples.

As reported in the work of Naccache *et al.* (13), the activated Rh–NaY zeolite exhibits a rhombic ESR spectrum at 77 K with g -values of $g_1 = 1.971$, $g_2 = 2.052$, and $g_3 = 2.091$. On adsorption of oxygen this spectrum changes into an axial spectrum with $g_{\parallel} = 2.051$ and $g_{\perp} = 1.931$. Using enriched $^{17}\text{O}_2$, Naccache *et al.* have shown that this new complex is not the superoxide ion O_2^- but is an oxygen adduct of the type Rh–O–O–Rh. The formation of this μ -peroxo adduct was found to be reversible under desorption–adsorption cycles with oxygen. This adduct changes irreversibly when exposed to water vapor; the axial ESR spectrum disappears and is replaced by a new rhombic spectrum with $g_1 = 1.981$, $g_2 = 2.016$, and $g_3 = 2.111$ as shown in Fig. 1. Note that direct adsorption of H_2O on activated Rh–Y without exposure to O_2 does not result in the new spectrum. The irreversible formation of this new spectrum suggests that the μ -peroxo adduct is split, presumably at the O–O bond, and that water is coordinated to a monomeric Rh(II) species. To reform the μ -peroxo adduct it was necessary to heat the sample in air at 773 K for several hours, followed by evacuation at 773 K and exposure to 100 Torr O_2 at room temperature or at 77 K.

Figure 2 shows the electron spin echo decay envelope recorded for Rh– $\text{NH}_4/\text{H}_2\text{O}$ by a two-pulse sequence. The theory and analysis of electron spin echoes have been well documented in the literature (20, 21). When suitable sequences of resonant microwave pulses are applied to a paramagnetic spin system microwave echoes are generated due to the reformation of macroscopic magnetization. In a two-pulse $\pi/2\text{--}\tau\text{--}\pi$ sequence, the echo is observed after a time interval τ after the second pulse while

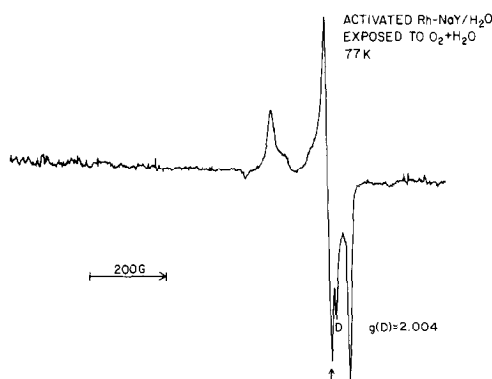


FIG. 1. ESR spectrum at 77 K of activated Rh–NaY with 1.0 wt% Rh exposed to O_2 and H_2O to form a Rh(II) species. D is a dewar background line which serves as a g marker. The arrow shows the field position at which ESE spectra were taken.

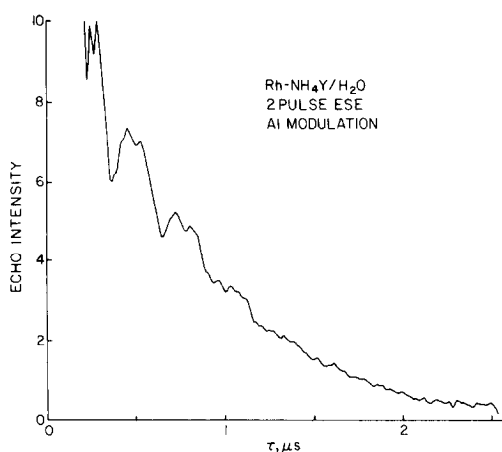


FIG. 2. Electron spin echo decay spectrum of the Rh(II) species in Rh-NH₄Y/H₂O with 3.1 wt% Rh at 4.2 K. The modulations shown are from ²⁷Al ($I = 5/2$).

in a three-pulse $\pi/2-\tau-\pi/2-T-\pi/2$ sequence the echo is observed at a time interval τ after the third pulse. Due to various relaxation mechanisms, the echoes decay as the pulse interval (τ or T) is swept resulting in an echo decay envelope.

Such echo decay envelopes often contain modulations resulting from weak hyperfine interactions between the paramagnetic spin and its surrounding magnetic nuclei. Analysis of such modulations can yield fairly accurate information on the distance between the paramagnetic spin and the interacting nuclei, on the number of such interacting nuclei and on the isotropic hyperfine coupling to these nuclei (22). Because the modulations are directly determined by the Larmor precessional frequencies of the interacting nuclei, it is easier to analyze the interaction with slower precessing deuterons (6.54 MHz at 10 kG) than that of faster precessing protons (42.5 MHz at 10 kG). It is also possible by a suitable choice of τ and pulse width to suppress one nuclear modulation frequency in a three-pulse spin echo experiment. Figure 3 shows such a three-pulse echo decay envelope where τ has been so chosen to minimize the aluminum modulation and to maximize the deuterium modulation.

Analysis of several such three-pulse

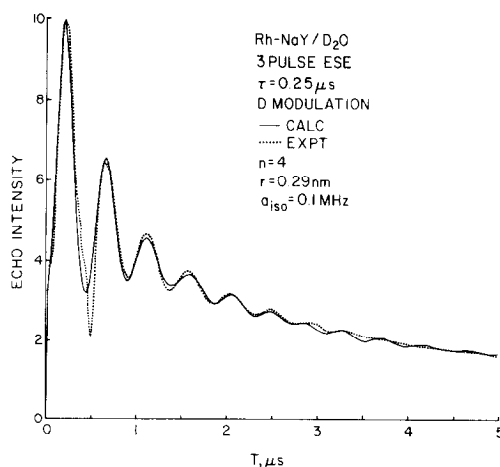


FIG. 3. Calculated and experimental three-pulse electron spin echo spectra for the Rh(II) species in Rh-NaY/D₂O with 1.0 wt% Rh at 4.2 K. The decay function used in the calculation is $g(T) = \exp[2.5 - 0.43T + 0.036T^2]$.

spectra indicates that Rh(II) interacts with four deuterons at 0.29 nm with an isotropic coupling (a_{iso}) of 0.1 MHz. This value of a_{iso} is in good agreement with the value obtained by fast Fourier transformation of the data (22). The number of deuterons is determined to the nearest integer, the a_{iso} value is determined to $\pm 10\%$, and the distance is determined to ± 0.01 nm. The four deuterons can be reasonably attributed to two water groups or to one water group and two hydroxyl groups if a water molecule is split. It is also possible to have four hydroxyl groups but this requires splitting of two adjacent waters which seems less probable. Naccache *et al.* (13) have suggested that the hydrated rhodium species is perhaps coordinated to one water and one hydroxyl group. However, simulations based on three interacting deuterons were not successful. The two most probable structures are given in Fig. 4.

The strong aluminum modulations shown in Fig. 2 could not be quantitatively analyzed because of the difficulties presented by aluminum's strong quadrupolar interaction. However, qualitatively the aluminum modulation shows that Rh(II) is fairly close to aluminum-rich sites such as the hexagon-

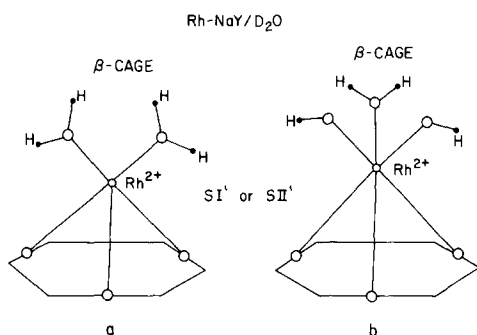


FIG. 4. Most probable structures for the Rh(II) species in activated Rh-NaY after exposure to O_2 and H_2O .

al prisms or the six-rings between the sodalite and super cages. The sites are designated SI for the center of a hexagonal prism, SI' for displacement from SI into a sodalite cage, SII for the center of a six-ring between the sodalite and super cages, and SII' for displacement from SII into the sodalite cage (23). Of these sites SI can probably be eliminated on the basis that the observed water or hydroxyl interaction distances are too close if Rh(II) were at that site. Site SII is acceptable for two coordinated water molecules in a trigonal bipyramidal coordination with three oxygens in the six-ring, but the g -factors do not support this geometry (24). The SI' or SII' sites in the sodalite cage are generally better suited for a higher coordination number associated with one water and two hydroxyl groups.

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