hydrogen is necessary to maintain the metal surface in such a condition which renders the formation of the relatively hydrogen-rich products such as isomers and methyl cyclopentane possible. It cannot be excluded that hydrogen *held by the catalyst* plays an active role in the surface complex for C_5-cyclization, similar to that suggested by Liberman (*12*) for the reverse reaction, i.e., the hydrogenolysis of the C_5 ring. In this case the assumption of diadsorbed species in the bond shift mechanism may be of secondary importance. Further work is being done on this problem.

These results are consistent with the concepts of Muller and Gault (*3*) for C_5-cyclization. It has been shown, however, that the very fine dispersion of the metal is not the only way to create active centers for this reaction; partial coverage of the surface of a carrier-free metal by hydrogen may lead to the same result. This, in turn, emphasizes that the same catalyst may show different types of activities according to the experimental conditions.

ACKNOWLEDGMENT

The authors thank Dr. S. J. Thomson of the University of Glasgow for valuable discussions.

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Received June 12, 1972

Valence State of Palladium in Y Zeolite*

All known stable square planar complexes of Pd(II) and Pt(II) are diamagnetic with low-spin d^8 configurations, but the corresponding complexes obtained by loss or gain of an electron should give d^7 or d^9 paramagnetic species possibly observable by ESR. There are only a few ESR studies about Pd ions reported in the literature. Pd(III) ions have been observed in various matrices (*1–3*) while ESR of Pd(I) has only been reported recently by γ-irradiation of single crystals of bis(acetylacetonato)palladium (II) (*4*), K_2PdCl_4 and $(NH_4)_2PdCl_4$ (*3, 5*) and also of metaphosphate glasses (*6*). On the other hand, palladium has been correspondingly little investigated [see, for instance, (*7*)].

Recently, zeolites have been used to obtain well-dispersed platinum catalysts (*8, 9*). It was shown (*9*) that tetrammine-platinum(II)-exchanged Y zeolite decomposed in oxygen prior to reduction gave well-dispersed platinum. In the present study the ESR technique has been used to follow the change of oxidation state of the cation in the case of tetrammine-palladium(II)-exchanged Y zeolite during decomposition in oxygen or *in vacuo*.

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* Presented by M.C. at the Chemical Society Autumn Meeting, Nottingham, 27 September 1972 and at the Symposium on "Role of Surface Charge in Reactions at Interfaces" Cork, 3 January 1973.

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Palladium was introduced into NaY zeolite by ion exchange from ammoniacal solution of $PdCl_2$. The structure of the palladium-exchanged Y zeolite has been studied in our laboratory (*11*). X-Ray evidence was found for palladium cations fixed at structural sites present in the zeolite framework. Moreover, chemical analysis left no doubt that ionic exchange had occurred. The resulting exchanged zeolite contained 12.5 Pd ions, 12.5 NH_4 ions and 18.5 Na ions per unit cell. The paramagnetic absorption of Pd has been investigated both at room temperature and 77°K using a V 4502 Varian spectrometer.

After treatment for 12 hr at 500°C, first under 160 Torr of oxygen and then under vacuum, two ESR signals were observed simultaneously

signal 1: $g_\perp = 2.10$, and $g_\parallel = 2.33$,
signal 2: $g_{\text{iso}} = 2.223$, $\Delta H_{\text{pp}} \simeq 16$ gauss.

The relative intensities depended upon the thickness of the catalyst bed in the 1 cm OD tube used for the heat treatment. Deep-bed calcined samples were dark brown and gave a stronger signal 1 while shallow-bed calcined samples, reddish brown in color, led to a stronger signal 2 or even to signal 2 alone. If the samples were treated at 500°C under oxygen, only signal 2 was observed, whatever the bed thickness (Fig. 1a). On the other hand, if the heat treatment was carried out under vacuum at 500°C, then only signal 1 was present, whatever the bed thickness (Fig. 1b).

Signal 1 was very oxygen sensitive and disappeared rapidly upon contact with O_2 at 200°C. Hydrogen had no effect on this signal at room temperature. Signal 2 was oxygen insensitive but was converted readily into signal 1 upon contact at room temperature with hydrogen.

The conditions of formation of species 1 (only *in vacuo*) and species 2 (in oxidizing atmosphere) as well as their behavior toward O_2 and H_2 allow us to assign species 1 to Pd(I) and species 2 to Pd(III).

The presence of both species 1 and 2 after the 500°C O_2–500°C vacuum heat treatment arises from the successive influence of oxygen and of ammonia, released from the zeolite, which reduces Pd(III) to Pd(I) at the same time as vacuum does. This is the reason why deep-bed calcined samples exhibited strong Pd(I) signals due to the important reducing power of ammonia released by heat treatment.

Moreover, theoretical considerations confirm the previous assignments. Pd(I) has a $4d^9$ configuration, similar to the d^9 configurations of Cu^{2+}, Ni^+ and Ag^{2+}. Consequently Cu^{2+}, Ni^+, Ag^{2+} and Pd^+ should give g values higher than the free electron g value, as observed in metaphosphate glass (*6*). Experimental g values for Pd(I) are shown in Table 1 and are in good agreement with the expected g values.

As the line width of signal 1 is temper-

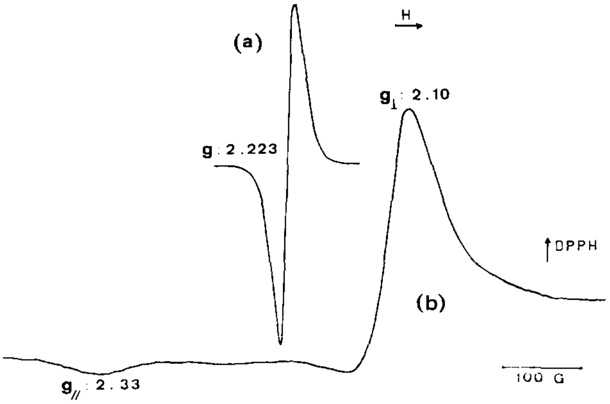

Fig. 1. ESR signal (9200 MHz and 77°K) of (a) sample heated in air at 500°C, Pd(III) ions; (b) sample heated *in vacuo* at 500°C, Pd(I) ions.

TABLE 1
ESR Parameters of Pd(I) Ions in Various Matrices

Species	Matrix	$g_\perp$	$g_\parallel$	Ref.
$Pd(I)(acac)_2^-$	$Pd(II)(acac)_2$	2.093[a]	2.517	*(4)*
$PdCl_4^{3-}$	K_2PdCl_4	2.084	2.516	*(3)*
		2.083	2.515	*(5)*
	$(NH_4)_2PdCl_4$	2.086	2.527	*(5)*
Pd(I)	Metaphosphate glass	2.095	2.34[b]	*(6)*
	NaY zeolite	2.10	2.33	This work

[a] Mean value of g_{xx} and g_{yy}.

[b] The $g_\parallel$ value was measured approximately with the magnetic field scale given in Ref. *(6)*.

ature independent, it can be concluded that it is not governed by the spin-lattice relaxation time. Due to the strong g anisotropy, Pd(I) ions are likely to undergo a strong axial crystal field produced by the zeolite framework.

Pd(III) has a $4d^7$ configuration and gives rise to isotropic lines *(1, 2)* or asymmetric lines with $g_\parallel = 2.012$ and $g = 2.149$ *(3)*. As can be observed from experimental results obtained for d^7 systems, a Jahn-Teller effect is to be expected in cubic or trigonal symmetry, giving a change from an isotropic to an anisotropic spectrum as the temperature is lowered *(10)*. Indeed, the line shape of the Pd(III) ESR signal is strongly temperature dependent, as it is not observed at room temperature.

The present results strongly suggest that palladium can be stabilized in the lattice framework in different oxidation states depending upon the activation conditions of the catalyst. Palladium ions introduced in NaY zeolite in the oxidation state (II) are converted into Pd(III) possibly by the following process:

$$2\,Pd^{2+} + H_2O + \tfrac{1}{2}\,O_2 \rightarrow 2[Pd^{3+}(OH)^-]^{2+}$$

On the other hand, formation of Pd(I) during a reducing treatment might result in the formation of trigonal aluminum atoms according to the scheme:

$$2\,NH_3 + 3\,O^{2-} \rightarrow N_2 + 3\,H_2O + 6e^-,$$
$$Pd(II) + e^- \rightarrow Pd(I).$$

A fuller account of the investigation on the valence states of Pd as well as their reactivity towards different gases will be reported elsewhere.

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Received July 19, 1972