Paramagnetic Metal Species on Highly Dispersed Rhodium/Polyphosphine Catalysts

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ESR active paramagnetic species were used as a probe for the description of the metal centers in highly dispersed rhodium/polyphosphine catalysts. Magnetically dilute Rh(0) centers were observed at high P/Rh_s (s = surface) ratios. Two different Rh(0) diluted species were detected ($g_1 = 2.085$, $g_2 = 2.000$; $g_1' = 2.045$, $g_2' = 2.008$, $g_3' = 1.975$) whose relative amounts vary with the P/Rh_s value. At lower P/Rh_s values, metal crystallites play a dominant role in giving broad unresolved signals. The metal particle size and the absolute Rh% are also related to the resonance shape. It is suggested that phosphine coordinates Rh centers, where a rhombic species corresponds to a higher number of coordinated phosphines. The results of the ESR investigation are in good agreement with previous studies on the same catalysts (G. Cocco, S. Enzo, F. Pina, and G. Strukul, *J. Catal.* **82**, 160, 1983) performed by SAXS, WAXS, TGA, TPR, and infrared study of CO adsorption.

INTRODUCTION

The existence of strong coordinative interactions between metal particles and the support can in principle, be a good method for the preparation of highly dispersed metal catalysts. Indeed, if supports containing ligands capable of stabilizing zerovalent metal species are used, the migration of the metal centers on the surface and the consequent formation of metal crystallites can be limited. This has been proved in the case of Rh metal catalysts supported on styrene–2% divinylbenzene copolymers containing phosphine groups (*1*).

We have previously reported (*1*) physicochemical characterization of these catalysts performed by X-ray scattering techniques (SAXS and WAXS), TGA, TPR, and by infrared study of CO adsorption. Since the dimensions of the metal particles in most samples was very small, it seemed to us that the use of spectroscopic techniques capable of identifying molecular species could be successfully employed to determine both the electronic state and the coordinative environment of the metal centers. With this in mind we performed an ESR investigation of these catalysts aimed at identifying paramagnetic Rh species on the surface.

EXPERIMENTAL

The preparation of polyphosphine supports (PolyPPh$_2$) involved the addition of THF solutions of LiPPh$_2$ to Merrifield Polymer Fluka (chloromethylated styrene–2% divinylbenzene copolymers available with various chlorine contents; beads, 200–400 mesh), according to the method of Relles and Schluenz (*2*). The preparation of the catalysts from [Rh(COD)Cl]$_2$ and PolyPPh$_2$ along with their physicochemical characterization has been reported in a previous paper (*1*). The main analytical data are reported in Table 1.

ESR spectra were recorded on a Varian E-109 spectrometer using quartz cells under Ar atmosphere. To avoid O$_2$ contamination, the catalysts were treated in flowing H$_2$ at 403 K for 3 hr before ESR investigation.

The spin concentrations of the magnetically dilute species were determined by

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TABLE 1

Analytical, Particle Size, and ESR Data of Rhodium/Polyphosphine Catalysts

Catalyst	P(%)	Rh(%)	Particle size (Å)	P/Rh$_s$	Type of spectrum[a]	A (G)	Number of paramagnetic centers (spin/g)
Rh-1	1.6	1.0	15	5.8	b		5.6 × 10^{11}
Rh-2	6.2	9.9	15	2.3	c		
Rh-3	1.7	0.6	17	10.7	b	20	2.9 × 10^{11}
Rh-4	1.7	1.6	19	4.3	c		
Rh-5	1.2	0.5	12	8.4	b	20	2.44 × 10^{11}
Rh-6	1.2	1.0	16	4.5	b	20	3.6 × 10^{11}
Rh-7	1.2	2.0	18	2.3	b	20	5.4 × 10^{11}
Rh-8	1.2	5.0	29	1.2	b		4.7 × 10^{11}
Rh-9	1.7	3.0	19	2.3	b		14.5 × 10^{11}
Rh-10	0.5	0.5	26	4.6	c		
Rh-11	0.5	1.0	29	2.4	c		
Rh-12	0.5	2.0	44	1.6	c		
Rh-13	0.5	5.0	67	0.9	a		
Rh-14		1.1	48		a		
Rh-15		6.8	83		a		

[a] For classification a, b, c, see text.

double integration of the area of the resonance lines. The reference area was the area of Varian weak pitch (10^{13} spin/cm). The sensitive region of the ESR cavity was 1 cm; the internal radius of the ESR tube was 1.5 mm. The apparent density of the catalysts was 0.5 g/cm^3.

Simulation of ESR spectra was performed by using a modified version of the SIM 14 A program (QCPE No. 265-1974). The experimental spectra were compared with the simulated ones by trial-and-error procedures.

RESULTS AND DISCUSSION

Fifteen rhodium/polyphosphine samples have been considered and studied in the solid state (Table 1). Different behaviors have been observed in connection with the following parameters: the P/Rh$_s$ (s = surface) ratio, the absolute Rh% and P%, and the metal particle size computed from the SAXS distribution function.

Three main groups of samples can be envisaged on the basis of their ESR behavior:

(a) Samples with low or zero P/Rh$_s$ values, which do not show ESR lines or show only broad unresolved resonances (Rh-13, Rh-14, Rh-15).

(b) Samples with high P/Rh$_s$ which show (Fig. 1) the lines typical of magnetically dilute species (Rh-1, Rh-3, Rh-5, Rh-6, Rh-7, Rh-8, Rh-9).

(c) Samples of P/Rh$_s$ values comparable to those mentioned in (b) where dilute species are poorly distinguished from the broad resonances of the undiluted ones (Rh-2, Rh-4, Rh-10, Rh-11, Rh-12).

All the observed ESR signals are attributed to Rh paramagnetic centers on the basis of the following considerations: (i) the supports do not show any signals when checked in the same experimental conditions as the catalysts; (ii) all signals are observed after reduction of the catalysts obtained from a diamagnetic Rh(I) precursor; (iii) the resolution of the spectra depends on Rh metal dilution as demonstrated by the observation that the signals broaden at low P/Rh$_s$ values and disappear if the polymeric support is not phosphinated (Rh-14, Rh-15); (iv) the resonances disappear at room temperature as expected for species with very
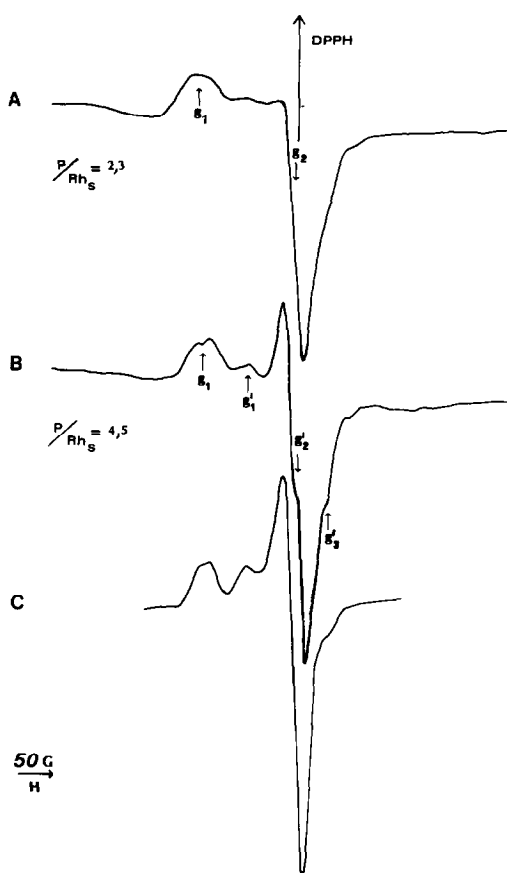
FIG. 1. X-Band ESR spectra recorded at 123 K: (A) Rh-7; (B) Rh-6; (C) computer simulation of spectrum B.

been overcome by computer simulation. The best fit has been obtained assuming a ratio axial/rhombic = 100 and using the parameters: $g_1 = 2.085$, $g_2 = 2.000$; $A_1 = 20$ G; $g_1' = 2.045$, $g_2' = 2.008$, $g_3' = 1.975$; linewidth $\sigma_1 = 18$ G, $\sigma_2 = 23$ G; $\sigma_1' = \sigma_2' = \sigma_3' = 20$ G; microwave frequency 9078 MHz.

Hyperfine coupling assignable to interaction with one Rh nucleus ($I = \frac{1}{2}$) has been observed in four cases (Fig. 1, Table 1).

It is worth noting that besides the resonances due to magnetically dilute species, a broad signal due to undiluted metal is always present in a quantity which is inversely dependent on the P/Rh_s ratio. The results of double integration reported in Table 1 show that magnetically dilute centers range from 0.8×10^{-6} to $5 \times 10^{-6}\%$ of the total supported Rh.

ESR active Rh compounds are rare examples in coordination chemistry and are predominantly Rh(II) (4). As for Rh(0), no unambiguous examples are reported, to our knowledge, except for the Rh(0) centers mentioned in an ESR study (5) of Rh in halide diamagnetic hosts. A comparison of our data with the g tensor components of the known Rh(II) complexes (4) shows that the values in our systems are very different. Moreover, signals become visible after reduction of the catalysts and cannot be observed if the polymeric support is not phosphinated (Rh-14, Rh-15).

These arguments suggest that the paramagnetic ESR active Rh(0) centers can be stabilized in connection with the presence of phosphine ligands on the support. Zerovalent electronic configuration of transition metal ions is well known to be stabilized by particular ligands such as phosphines. In the present case we infer that phosphines lie in the coordination field of Rh. This is not unexpected since a coordinative interaction of the phosphine groups with the metal surface has been identified in a previous paper (1) by infrared spectroscopy after CO adsorption.

The ESR properties of all the magnetically dilute species observed in our cata-

short spin-lattice relaxation times like the $4d$ group elements (3).

The resonance lines in Fig. 1, which refer to Rh-6 and Rh-7, are strongly temperature dependent and the magnetic anisotropy is clearly resolved at 123 K.

Two main species whose relative amounts are dependent on the P/Rh_s ratio are visible. The species which dominates at lower ratios shows axial symmetry, while the other species more probably has rhombic symmetry. The values of the g tensor components of the axial species ($g_1 = 2.085$, $g_2 = 2.000$) can be assigned to parallel and perpendicular resonance, respectively. As for the rhombic species, while g_1' and g_3' are clearly distinguished, g_2' is difficult to separate from g_2. This problem has

lysts are similar to those of mononuclear metal compounds. This is consistent with the hyperfine coupling observed in four samples. However, we cannot exclude, on the basis of ESR data, that paramagnetic metal clusters (6) are present on the surface. In this case their nuclearity should be very low, since ESR resonances have been detected. Prior knowledge of the coordination geometry is required to assign the ground state configuration of the Rh(0) species. However, if we consider the species having axial magnetic symmetry, the only ground state configuration which is in agreement with the trend of g values ($g_\parallel >$ $g_\perp \geq 2$) is the one corresponding to the unpaired electron of Rh(0) in the $d_{x^2-y^2}$ orbital. As for the rhombic species, the symmetry becomes too low to suggest the location of the unpaired electron. However, in our opinion, the two observed paramagnetic metal species have the same oxidation state, while they differ in the ligand field around the Rh centers. Since the average of g values (g_{av}) decreases from the axial to the rhombic species and the rhombic species appears to be stabilized by higher P/Rh_s values, we suggest that the latter species has a higher number of coordinated phosphines and a larger electron density on the metal. The decrease of g_{av} could indeed be due either to a decrease of the spin-orbit coupling constant or/and to an increase of the ligand field splitting energies.

As for the above cited group (c) samples which show ESR spectra not dependent on the P/Rh_s parameter, their behavior can be explained as follows: Rh-2 and Rh-11 have the same P/Rh_s values as Rh-7 and Rh-9, but Rh-2 contains such a large amount of metal that spin–spin interactions should be much more extended. As for Rh-11, the difference could be related to the larger particle size with respect to Rh-7 and Rh-9. Similar arguments can apply to Rh-4 and Rh-10 when compared to Rh-6. Finally, the particle size effect in Rh-12 compared to Rh-8

becomes overwhelming despite the more favorable metal content.

Though relative to a small number of sites, the coordinative environment and the electronic state of the metal centers as deduced from the ESR investigation are in good agreement with the already mentioned infrared results, which refer to the overall metal surface. Moreover, the increasing electron density on Rh sites observed when increasing the phosphine contents is a direct proof of what we have tentatively suggested to explain other experimental observations on the reactivity of these catalysts, i.e., the difference in activation energy between phosphinated and nonphosphinated catalysts in ethylene hydrogenation (7) and the selectivity in product distribution in the hydroisomerization of 1,5-cyclooctadiene (8).

In the present case ESR has proved to be an interesting probe for the description of the metal surface, and we believe that further studies in this field might prove this technique to be a useful tool for the characterization of dispersed metal catalysts.

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