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Electron Spin Resonance Observation of Platinum and Iridium Chloride Species on Reforming Catalysts

Elucidation of the nature of platinum in Pt–alumina naphtha reforming catalysts has attracted considerable attention during the past two decades. Even though the mechanistic aspects of the reforming reaction are known in some detail, the structure and identity of the active platinum species on commercial reforming catalysts taking part in typical reactions like dehydrocyclization, isomerization and dehydrogenation are still not understood clearly. For example, even though the existence of a non-zero valent platinum species active in the dehydrocyclization of *n*-heptane had been postulated by many authors (*1–3*), no *in situ* experimental identification of such a moiety has so far been reported. In the present study, we report the observation by electron spin resonance spectroscopy of a chloroplatinum species in Pt–alumina and Pt–Ir–alumina catalysts as well as a chloroiridium species on Ir–alumina.

The catalysts are described in Table 1. They were prepared from the corresponding chloroplatinic and/or chloroiridic acids and had a similar chloride content of about 0.9% by wt. The catalysts, contained in special ESR tubes attached to a conventional high vacuum adsorption system, were subjected to the pretreatments shown in Table 1, sealed *in situ* and then transferred to a Varian E 4 EPR spectrometer for measurement of the spectra at 295°K. DPPH was used as the *g* calibrant. The spectra are shown in Figs. 1 and 2. The essential features of the spectra are summarized in Table 1.

The fact that under varying conditions of pretreatments both the Pt–alumina and Pt–Ir–alumina systems exhibit identical spectra (compare the A_{av} values for M_1–B_1, M_2–B_2, and M_3–B_3 in Table 1 as well as the almost identical shape of the lines for the above pairs of samples in Fig. 1), suggests strongly that the same species is involved in both the cases. Samples of alumina not containing chlorine together with Pt (or Ir) did not exhibit any ESR spectra at all. The species responsible for the spectra in Fig. 1, for example, is thus probably either a moiety of chlorine, like Cl_2^- which is stable only in the presence of platinum or a chloroplatinum species. Similar arguments apply to the Ir–alumina system in Fig. 2. It should be noted that this species is formed on calcination of the impregnated catalyst at 500°C and does not undergo any further structural change during subsequent evacuation and reduction treatments (Table 1 and Fig. 1).

The chlorine isotopes ^{35}Cl and ^{37}Cl possess a nuclear spin of $\frac{3}{2}$ while platinum atoms of mass 195 (natural abundance, 33.7%) possess a nuclear spin of $\frac{1}{2}$. The occurrence of seven approximately equally spaced lines in the ESR spectra (Figs. 1 and 2) immediately suggests that these arise from an unpaired electron interacting with two chlorine nuclei of spin, $\frac{3}{2}$. Comparison of the observed values of the hyperfine coupling constants (44–47 Oe, Table 1) with those quoted in the literature for Cl_2^-, however, leads to the conclusion that the species responsible for the spectra in Fig. 1 cannot be Cl_2^-. For example, Castner and Kanzig (*4*) reported the following values of the hyperfine coupling constants, *A* (Oe), for Cl_2^- in the matrices mentioned below:

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TABLE 1

ESR Spectra of Reforming Catalysts

Symbol	Catalysts description	Pretreatment	Features of ESR spectra	
			g_{av}	A_{av} (Oe)[a]
M_1	0.35% $Pt-Al_2O_3$ calcined at 500°C	Evacuation at 25°C	1.993	44
B_1	0.35% Pt–0.05% $Ir-Al_2O_3$, calcined at 500°C	Evacuation at 25°C	1.995	44
M_2	Same as M_1	Evacuation at 500°C	1.989	46
B_2	Same as B_1	Evacuation at 500°C	1.988	47
M_3	Same as M_1	Reduction at 500°C followed by evacuation at 500°C	1.988	46
B_3	Same as B_1	Same as for M_3	1.988	46
Ir_1	0.9% $Ir-Al_2O_3$ calcined at 500°C	Evacuation at 25°C	1.997	69
Ir_2	Same as Ir_1	Evacuation at 500°C	2.003	76
Ir_3	Same as Ir_1	Same as for M_3	2.001	78

[a] Average values of g and the hyperfine coupling constant.

102 (silica gel), 98 (NaCl), 101.4 (KCl), 101 (benzene) and 99 (cyclohexane), respectively. The observed value of 46 Oe is thus probably caused by a species containing at least two chlorine atoms in intimate interaction with at least one Pt (or Ir– in the case of Fig. 2) atom.

Now, in the preparation of M_1, for example, chloroplatinic acid is deposited on alumina (containing about 0.6% by wt of chlorine) the product dried at 110° and calcined at 500°C. The observed chloroplatinum species must have arisen by decomposition of the $[PtCl_6]^{2-}$ ion or as a product of its reaction with the alumina surface. $[PtCl_6]^{2-}$ ion (Pt^{4+}) is diamagnetic and does not exhibit any ESR signal (*5*). $PtCl_5^{2-}$ ion (Pt^{3+}) has been identified as a radical formed by gamma ray and electron irradiation of K_2PtCl_6 single crystals at 77°K (*5*). At 125°K it shows an ESR spectrum consisting of four lines due to hyperfine interaction of an electron with one platinum and one chlorine nuclei. It does not exhibit any ESR spectra at room temperature as is to be expected for a d^7 system. Moreover, its g values ($g_{zz} = 1.942$, $g_{xx} = 2.417$, $g_{yy} = 2.386$) and A values [$A(^{35,37}Cl) = 56.8$ Oe] are quite different from those noted in our study (Table 1). The $(PtCl_4)_2^{3-}$ ion (Pt^{2+}) had also been observed in the above study (*5*) to exhibit an ESR spectrum of six lines due to a radical containing two magnetically equivalent platinum nuclei. Again the ESR signals of this radical are observed only at 77°K and disappear on warming to room temperature in agreement with the expectations for d^6 systems which usually have short spin–lattice relaxation times and hence exhibit ESR spectra only at very low temperatures. In addition, the g values, namely $g = 1.771$, $g = 2.723$ are quite different from those in the present study. Ten lines with a hyperfine coupling constant of $A = 11.5$ Oe were observed for the $PtCl_3^{2-}$ ion (Pt^+). Our ESR spectra consisting of seven lines are, thus, probably caused by $PtCl_2^-$ wherein Pt has a d^9 configuration. The ground state of the free ion is $^5D_{\frac{5}{2}}$ and such systems (like Cu^{2+}, for example) have long spin–lattice relaxation times. The fact that

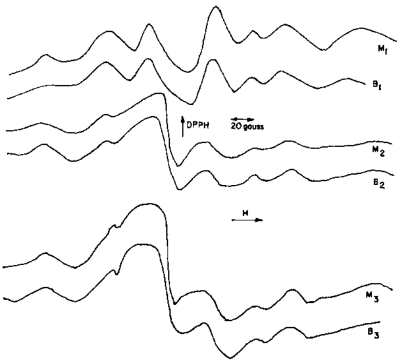

FIG. 1. ESR spectra of the Pt–alumina and Pt–Ir–alumina samples described in Table 1.

the spectra are observable even at room temperature suggests that the two Pt–Cl bonds are not colinear, being probably bent. In this lower symmetric configuration, the ground state will be a Kramer's doublet which in turn will account for the ready observation of the spectra at room temperature. In the case of samples Ir_1, Ir_2, and Ir_3, whose spectra also consist of seven lines (Fig. 2) but with different values of g_{av} and A_{av} (Table 1), a similar chloroiridium species is thought to be responsible for the results.

Some plausible models of the $[PtCl_2]^-$, species as it occurs on the alumina surface are shown in Fig. 3A. There are three structural aspects of the Pt atoms in such species which merit attention: (a) Due to their "anchoring" through the chlorine atoms in the alumina structure, such Pt atoms should be less susceptible to sintering compared to those Pt atoms in metal clusters. (b) Being highly exposed to the adsorbing hydrocarbon molecule, its ability to coordinate with multiple bonds to different parts of the same molecule will be much higher than surface atoms in a metal crystallite. (c) Being an isolated ion, its electronic properties will be quite different from the neutral metal atoms in a cluster. Especially, those reactions for which there is a net transfer of electrons from the adsorbed hydrocarbon molecule to Pt during the rate determining step will be selectively enhanced at such sites.

An alternative bonding of these $[PtCl_2]^-$ species to the alumina surface is through two oxygen bridges with the two chlorine atoms projecting away from the surface. However, in view of the fact, that the support used in our study was a chlorided alumina, the occurrence of species like those in Fig. 3 is more likely than those involving oxygen bridges.

From a study of the isomerization and dehydrocyclization of hexanes, Muller and Gault (*6*) and Anderson *et al.* (*7*) had arrived at an important conclusion that the dehydrocyclization process probably involves a single metal atom. A *1.1.5*-triadsorbed species (Fig. 3B) was suggested as the precursor for dehydrocyclization over highly dispersed Pt catalysts (*6*). This structure presumes, (a) that the Pt atom is able to accommodate both the σ and π electrons of carbon atoms 1 and 5 in its bonding orbitals and (b) that the hydrocarbon molecule is not sterically hindered while being multiply bonded to the metal atom. We suggest that the Pt atom in the chloroplatinum complex (Fig. 3A) fulfills these criteria and that it is the active site for the dehydrocyclization reaction. The direct correlation between the dehydrocyclization activity and the concentration of "soluble chloroplatinum complex" observed by McHenry *et al.* (*1*) for a series of

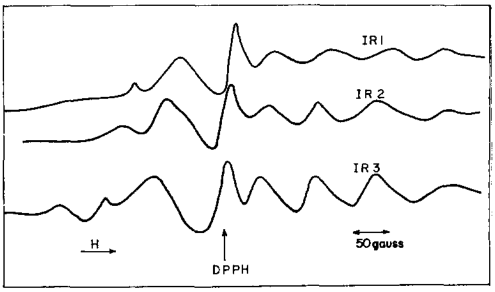

FIG. 2. ESR spectra of Ir–alumina samples, see Table 1 for description of the samples.

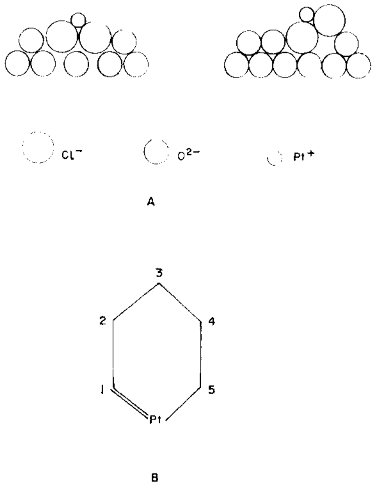

FIG. 3. Surface species: (A) The chloroplatinum complex; (B) the procursor species for dehydrocyclization according to Muller and Gault (*6*).

reforming catalysts further supports our hypothesis since the $[PtCl_2]^-$ species is expected to be soluble in acetylacetone as well as in HF, whereas, metallic platinum is not soluble in both these solvents (*1*).

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