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Electron Paramagnetic Resonance (EPR) Investigations on Silica-Supported Silver Catalysts and Adsorbed Oxygen Species

In a number of publications (*1–3*) it has been postulated that diatomic and monoatomic oxygen species coexist at the surface of a silver catalyst during ethylene oxidation and that they play a determining rôle in, respectively, the formation of ethylene oxide and the complete oxidation of the hydrocarbon. A direct identification of the adsorbed oxygen species by spectroscopic techniques is therefore of interest. A few studies involving ir spectroscopy have been published (2–4) but, to our knowledge, EPR has not been used extensively (*5–7*). The object of this Note is to report preliminary EPR data obtained when a silica-supported catalyst is maintained under conditions close to that of the catalytic reaction.

The catalyst, containing 2% Ag by weight, was prepared by first contacting silica (Cab-O-Sil) with an aqueous solution of ammoniacal silver nitrate at room temperature (*8*). The solid was then filtered, washed, dried, crushed and sieved. Before use, the samples were treated by flowing helium at 473 K (sample I) and reduced at 523 K in a hydrogen flow (50 ml/min) for 12 hr and further contacted with a helium flow at 473 K for 1 hr (sample II). In some experiments, the reduced catalyst (sample II) was oxidized in flowing oxygen (p_{O_2} = 18 Torr) at 473 K during 12 hr and then treated again by flowing helium to remove gaseous oxygen and thus avoid the broadening effect of paramagnetic oxygen on the EPR spectrum (sample III). In other experiments, the reduced sample was used as a catalyst for ethylene oxidation at 473 K (p_{ethylene} = 7 Torr; p_{O_2} = 10 Torr). After reaction, the apparatus was again flushed by helium gas to remove reactants and products (sample IV). All experiments were performed in a differential microreactor equipped with side EPR tubes where the catalyst could be transferred under helium, after a given experiment. The tubes were then sealed off and placed in the dual cavity of an E-9 Varian spectrometer, used in either X or Q band. Spectra were recorded at liquid nitrogen temperature.

The EPR spectra of all samples (I to IV) exhibit the same nearly symmetrical line at $g = 2.0024$. Its width is, in all cases, close to 6.0 Oe. However, the intensity of the signal is a function of the treatment conditions (Table 1). Moreover, it has been observed that the intensity of the signal decreases if, in the case of sample II, the reduction temperature is increased from 473 to 673 K. Similar results were also obtained with Ag–Na Y zeolites. It is worth noting that no hyperfine coupling due to Ag nuclei ($I = \frac{1}{2}$, $A_0 = 650$ Oe) (*9*), has been detected: silver atoms in the investigated samples form particles and not small aggregates. Electron micrographs have indicated that in samples II to IV, the mean particle diameter is constant and equal to 53 Å.

Similar signals have been recently reported for small silver particles in different matrices such as CO_2, C_6H_6 and $C_{18}H_{38}$ (*10*). They have been assigned to conduc-

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TABLE 1

Variations of Intensity of the EPR Line ($g = 2.0024$) of Silver Particles on SiO_2 as a Function of Treatment Conditions (See Text)

Samples:	I	II	III	IV
EPR line intensities (arbitrary units)	22	100	54	82

tion electrons in silver particles which are small enough for the quantum size effect to take place (*11–13*). For these particles, the boundary conditions imposed on the conduction electrons cause the conduction energy levels to become discrete and EPR signals can be observed if the separation between adjacent levels becomes larger than the Zeeman energy, $\hbar\omega_z$ and if the following condition is satisfied: $\delta \gg h/\tau$ where τ is the relaxation time given by Elliott (*14*). In the case of silver both conditions are satisfied for crystals of size smaller than 70 Å (*10*).

The signal which has been detected in the spectra of samples I to IV is therefore attributed to conduction electrons. The decrease of the signal intensity which is observed when the reduction temperature increases is moreover explained by the formation of larger particles at a higher temperature. This interpretation has been further confirmed by the absence of this signal in the spectrum of similarly prepared silica supported silver catalyst containing larger metal particles (350 Å) (*8*). The last result moreover indicates that the signal cannot be attributed to carbonaceous impurities.

The intensity of the signal recorded for sample II, obtained by integration and comparison with a Varian pitch reference, is $\simeq 10^{16}$ spins/g of catalyst. This value is close to half the number of silver particles per gram of catalyst [1.3×10^{16}, assuming that all silver atoms, 1.2×10^{20} Ag atoms/g, are distributed in cubooctahedra of 53 Å diameter, thus containing 4800 atoms/particle (15)] and therefore agrees with the theoretical assumption that, in small metal particles, there is one paramagnetic center per particle with an odd number of atoms and no paramagnetic center for an even number of atoms (*16*).

From the relative changes of intensity presented in Table 1 for the different samples, the following conclusions can be drawn:

i.) The starting material (sample I) is slightly reduced, presumably by the photons of daylight.

ii.) The oxygen treatment at 473 K (sample III) produces partial oxidation (46%) of silver particles.

iii.) In the presence of reaction mixtures, the silver particles in sample IV remain partly oxidized (18%) but less than after an oxygen treatment (sample III).

The spectra of oxygenated catalysts and particularly sample III did not exhibit any signal which could be attributed to oxygen species. Adsorption of oxygen, at 473 K, on these catalysts does not produce paramagnetic species such as O_2^-, at variance with previously published results on the oxygen adsorption on silver at 160 (*7*) or 300 K (*6*). In order to characterize the diamagnetic oxygen species, the existence of which is demonstrated in Table 1 by the decrease of the EPR signal after oxygen treatment, irradiation of sample III, by γ rays from a ^{60}Co source, was performed at liquid nitrogen temperature. It has been shown (*17*) that irradiation can ionize diamagnetic species into paramagnetic ones which are characteristic of the precursors.

The EPR spectra of sample III and for comparison purposes, of Cab-O-Sil silica, after γ irradiation at 77 K, are presented in Fig. 1. The spectrum of the oxidized catalyst presents, at low magnetic fields, three bumps at $g_1 = 2.058$, 2.038 and 2.028 which are absent from the spectrum of pure Cab-O-Sil. They correspond to the $g_{\parallel}$ components of three distinct signals whose

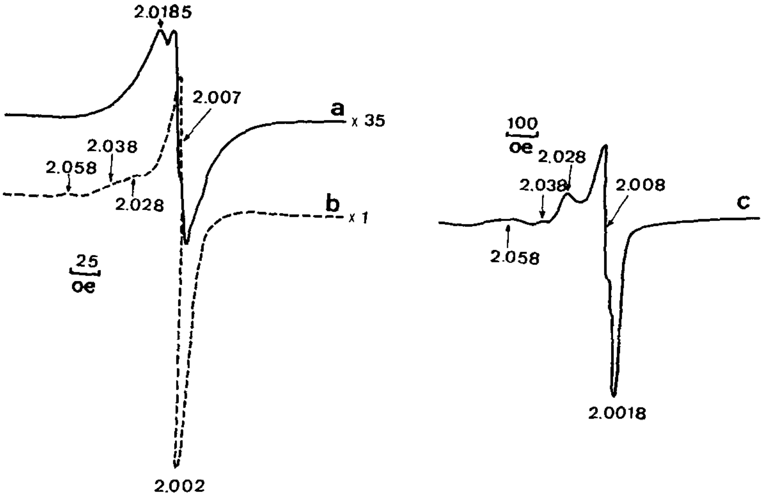

FIG. 1. EPR spectra of catalysts treated at 473 K under oxygen and then flushed with helium to remove physisorbed oxygen before irradiation. (a) Pure Cab-O-Sil in X band (the spectrum is due to the overlapping of V- and F-type signals) (*18*); (b) silver/Cab-O-Sil in X band; (c) silver/Cab-O-Sil in Q band (all samples were γ-irradiated ($\simeq$1 mrad) at 77 K).

$g_\perp$ components are close to g_e, presumably at $g = 2.008$ and 2.0018, though overlapping does not allow one to conclude unambiguously. Such EPR signals are typical of O_2^- ions adsorbed on powder catalysts (*19*, *20*). No signal due to Ag^{2+} ions (d^9) was observed (*7*).

During a study of O_2^- ions in Y-type zeolites with different polyvalent cations, Kasai (*20*) has shown that the Π^* antibonding orbital degeneracy is lifted by the cation to which the O_2^- species is bonded and that the Π^* energy separation, Δ, between Π_x^* and Π_y^* is proportional to the cation charge, Π_x^* bearing the unpaired electron and Π_y^* being fully occupied. As is well known (*21*), $\Delta g_z \alpha 2\lambda/\Delta$ is large and particularly sensitive to this degeneracy release, whereas $\Delta g_y \alpha 2\lambda/E$ and mainly $\Delta g_x \alpha \lambda^2/\Delta E$ (E being the σ–Π_x^* energy separation are small and not very much affected. The z axis lies along the interatomic O–O bond. The experimental three values of g_z can thus be assigned to O_2^- ions subjected to a double, triple or quadruple positive charge. Since only monovalent cations (Ag^+) are present in the investigated system, it is possible to suggest tentatively that the electric charges arise from oxidized silver ensembles Ag_2, Ag_3 and Ag_4, assuming that the effect of such charged ensembles on the Π^* degeneracy release is identical to that for single cations. This conclusion is in agreement with previous hypotheses (*2*, *22*).

The species corresponding to $g_z = 2.028$ could also be attributed to O_2^- ions adsorbed on silica (Si^{4+}) (*19*). However, Fig. 1 shows that silver must be present for these species to exist in our experimental conditions, but since induction by the presence of silver ions could occur, as was observed for Mo^{5+}/Al_2O_3 catalysts (*23*), this possibility is not unambiguously ruled out.

The observed signals could also be tentatively assigned to V-type centers involving monoatomic oxygen species. The presence of ionically bonded O^- species is however ruled out since the corresponding EPR signal is characterized by $g_\parallel \simeq g_e < g_\perp$ (*24*). Covalently bonded species of the Ag–O–Ag type would yield a EPR signal with $g_\parallel > g_\perp \simeq g_e$ (*17*). Interaction with silver nuclei ($I = \frac{1}{2}$) would be likely to introduce an hyperfine structure in the spectrum as observed for Al–O–Al entities (*25*). A triplet hyperfine structure or at least a broad signal, if the hyperfine structure is unresolved, would be thus expected. Such spectra are not detected in Fig. 1. The presence of monoatomic oxygen species, though it cannot be unambiguously ruled out, is therefore unlikely.

In conclusion, it has been shown in this Note that in a silica-supported silver catalyst, only part of the metal is oxidized, at 473 K, by oxygen or during ethylene oxidation. The presence of two or three oxygen species associated with silver has been demonstrated. These species are diamagnetic. It has been postulated that they correspond to diatomic oxygen species bonded to two, three or four oxidized silver atoms. Further work using ^{17}O enriched oxygen is in progress to identify these species.

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Antoine Abou-Kais[1]
Milad Jarjoui
Jacques C. Vedrine
Pierre C. Gravelle

Institut de Recherches sur la catalyse, C.N.R.S.
79, Boulevard du 11 Novembre 1918
69626 Villeurbanne Cedex, France

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[1] Permanent address: Facultè des Sciences, II, Université Libanaise, Mansourieh, Liban, C.N.R.S. Libanais.