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# EPR Study of Osmium Species Derived from $Os_3(CO)_{12}$ Clusters Supported on Alumina

Osmium catalysts prepared by attachment of $Os_3(CO)_{12}$ complexes to the surface of $Al_2O_3$ have been studied by one of us previously and the results reported (*1, 2*). It was shown that under thermal treatment at temperatures higher than 470 K degradation of the osmium clusters leads to the formation of surface mononuclear tri- and dicarbonyl osmium complexes in which the oxidation state of osmium was suggested to be equal to 2+ (*2–4*). The goal of this present research is to understand whether $Os^+$ and $Os^{3+}$ ions could also be formed under such treatment. These ions have one unpaired electron in the low spin state (electronic configuration $5d^7$ and $5d^5$, respectively). Therefore they should be observable by EPR. In addition we also studied the samples reduced and oxidized under more severe treatments.

To increase the sensitivity of the EPR technique we have used the experimental fact that EPR spectra of surface carbonyl complexes of noble metal ions are considerably narrower than those of the complexes of the same ions without CO molecules in their coordination sphere (*5–7*).

The samples have been prepared by immobilization under $N_2$ of $Os_3(CO)_{12}$ complexes on the surface of $\gamma$-$Al_2O_3$ according to the method described earlier (*1*). They contained 0.78 wt% of osmium. After preparation the samples were stored in dry $N_2$, but were contacted with air before thermal treatment.

Thermal treatments of the samples were carried out *in situ* in quartz ampoules in which the EPR spectra were also measured. The ampoules were designed in such a way that measurements could be made without the presence of air. In all cases adsorption of CO (7–13 kPa) at room temperature was carried out before EPR measurements.

The EPR spectra were recorded at 77 K in the X-band, and $g$-values were determined with an accuracy of 0.001 with respect to a standard DPPH sample with $g = 2.0036$. The amount of ions was determined by integration of the EPR spectra and comparison with a standard sample of $CuCl_2 \cdot 2H_2O$.

The results and their interpretation are described in the following paragraphs.

*A. Initial and reduced samples.* Both evacuation at 300 K and reduction of initial samples by CO or $H_2$ at 670 K did not result in the appearance of any EPR signal. Even after CO adsorption at 300 K no EPR signal could be observed. This indicates that there are no paramagnetic osmium ions present in the initial and reduced catalysts which can be observed by the EPR method at 77 K. This result is in good agreement with the data reported previously (*2–4*), according to which one could expect zero-valent osmium species in the fresh sample and $Os^{2+}$ carbonyl complexes after CO treatment at 670 K.

*B. Thermoevacuated samples.* Initial samples treated in vacuum ($10^{-1}$ Pa, 1 h, 520 K) show an EPR signal (Signal I) with $g_\perp = 2.004$ and $g_\parallel = 2.032$ after CO adsorption at room temperature (Fig. 1a). The intensity of the signal corresponds to 0.1–0.3% of the total osmium in the sample.

Adsorption of CO molecules on samples evacuated at 720 K results in a slightly anisotropic signal (Signal II, $g = 2.003$) with an intensity corresponding to about 0.5–1% of total osmium (Fig. 1b).

The samples evacuated at 870 K show

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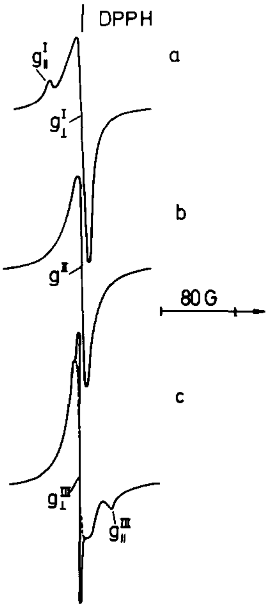

FIG 1 EPR spectra of osmium species supported on $\gamma$-$Al_2O_3$ (for treatment conditions see text)

before CO adsorption a narrow isotropic line ($\Delta H = 3$ G, $g = 2\ 003$) which probably belongs to a defect of $Al_2O_3$ (the isotropic $g$-tensor and the small linewidth do not allow us to ascribe it to osmium ions) It has been shown earlier (*8*, *9*) that thermoevacuation or reduction of $Al_2O_3$ leads to the appearance of the same line Adsorption of CO at room temperature gives rise to the appearance of a new anisotropic signal (Signal III, $g_{\perp} = 2\ 003$, $g_{\parallel} = 1\ 977$) (Fig 1c) which is observed simultaneously with the signal of the defect The intensity of the signal corresponds to 1–2% of total osmium

Taking into account that osmium in the initial catalysts has a valence state of zero and that the main part of the osmium ions in the samples treated in vacuum at temperatures higher than 470 K is divalent (*2–4*), the above data allow us to assign Signal I to a surface carbonyl complex of intermediate monovalent osmium ions $(O^{2-})_mOs^{+}(CO)_n$ At a higher temperature of evacuation these ions are oxidized to higher valence states This leads to the disappearance of Signal I

Signals II and III seem to belong to carbonyl complexes of paramagnetic osmium ions of higher valence states than 2+, most probably, 3+ A small amount of these ions can be formed at high temperatures of evacuation as a result of further oxidation of $Os^{2+}$ ions

The value of the anisotropy of the $g$-tensor of Signals I and III is in good agreement with the data reported for other surface carbonyl complexes of noble metal ions (*5–7*) Signal II has less anisotropy than Signals I and III, this allows us to ascribe it to some defect of $Al_2O_3$ interacting with CO molecules The difference between the shapes of Signals II and III, if they both belong to $Os^{3+}$ ions, may be caused by a different coordination of these ions These surface carbonyls of $Os^{+}$ and $Os^{3+}$ ions have not been observed previously by ir spectroscopy presumably because of the significantly lower sensitivity of that technique as compared to the EPR method

Unfortunately, the assignment of Os ions by hyperfine splitting caused by the $^{189}Os$ isotope ($I = 3/2$) is impossible since the intensity of the corresponding lines is too low (natural abundance of $^{189}Os$ 16%)

*C Oxidized samples* Oxidation (420–470 K, 13 kPa $O_2$, 1 h) of the thermoevacuated (520 K) samples leads to the disappearance of Signal I and appearance of Signal II (as with the thermoevacuated samples, the EPR spectra were recorded after adsorption of CO molecules) The intensity of Signal II in such oxidized samples is 2–3 times higher than that in the samples thermoevacuated at 720 K Thermoevacuation and subsequent oxidation at lower or higher temperatures lead to the appearance of a less intense signal There are no EPR signals in the samples oxidized at room temperature or in the temperature range 570–620 K

Heating of samples which were oxidized at 420 K in CO atmosphere at 420–470 K, or evacuation at 720 K leads to the disappearance of Signal II and appearance of Signal I Its intensity is 50–100 times higher than that of the samples thermoevacuated at 520 K and corresponds to about 10–12% of total osmium content Signal I disappears after further heating in CO at 720 K

These data support the above conclusion about the valence state of Os in the thermoevacuated samples They show that the oxidation of the $Os^+$ ions (Signal I) at 420 K leads to the formation of $Os^{3+}$ ions (Signal II), and at higher temperatures of oxidation $Os^{3+}$ ions are oxidized further to some nonparamagnetic state Under these conditions the formation of $Os^{3+}$ ions, which are characterized by Signal III, does not take place, apparently because these ions are more coordinatively unsaturated and could therefore be more easily oxidized by oxygen At the same time, the reduction in CO (420–470 K) of the samples containing mainly $Os^{2+}$ and a small amount of $Os^{3+}$ leads to the formation of $Os^+$ ions (Signal I) The $Os^+$ ions disappear under more severe conditions of reduction This means that the $Os^+$ ions are intermediate in the course of reduction–oxidation processes of the catalysts, but the main part of the osmium in the samples is in a diamagnetic form

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