Surface chemistry of noble metal complexes anchored from cationic complexes on a graphitised carbon support

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The adsorption and chemical transformations of ammonia complexes of Pd, Pt, Rh and Ir on the surface of a modified carbon support were studied by X-ray photoelectron spectroscopy.

Porous carbon materials are widely used for the preparation of metal-supported catalysts, particularly for liquid-phase processes. A new generation of graphite-like materials expands further the application of carbon supports. Among them, a 'Sibunit' mesoporous graphite-like carbon attracts particular attention because of its chemical inertness, mechanical strength, and high surface area (200–600 m^2 g^{-1}).[1] Several studies have been devoted to researching noble metal deposition on the carbon surface by ion exchange, since this technique allows the preparation of highly dispersed supported metal catalysts.[2–4]

However, most studies performed so far have focused only on the preparation of catalysts by ion exchange with anionic metal complexes like H_2PdCl_4, $HAuCl_4$, and H_2PtCl_6. The main disadvantage of this approach is the reduction of the anionic complexes in the course of ion exchange resulting in an uncontrolled deposition of reduced metal species. As a result, the metal dispersion becomes poor and the amount and distribution of the deposited metal cannot be controlled.[3,4]

Our preliminary experiments with cationic complexes demonstrated that the ion-exchange capacity of the parent Sibunit is negligible (Table 1). Therefore, the aim of this study was an attempt to modify the Sibunit surface in order to increase its exchange capacity towards cationic complexes and to study their deposition with the final goal of preparing highly dispersed metal supported catalysts.

The presence of active oxygen-containing groups on the surface of the carbon material is a prerequisite for the efficiency of ion exchange of cationic complexes.[5] Therefore, before ion exchange, Sibunit (5 g) was treated with 150 ml of an aqueous $KMnO_4$ solution (0.2 mol dm^{-3}) for 3 h at 80 °C. The resulting material was rinsed with distilled water to pH 7. After that, the Sibunit was treated with 4 M HCl overnight at room temperature. Next, the Sibunit was exhaustively washed with distilled water until the sample became free of nitrate and manganese ions, as evidenced by XPS.

Table 1 Ion-exchange capacity of Sibunit towards noble metal complexes.

Sibunit	Complex	Concentration of the complex in solution/mol dm^{-3}	Exchange capacity[a]/ mmol g^{-1}
parent	$[Pd(NH_3)_4](NO_3)_2$	0.01	< 0.005
parent	$[Pt(NH_3)_4]Cl_2$	0.01	< 0.005
modified	$[Pd(NH_3)_4](NO_3)_2$	0.01	0.34
modified	$[Pd(NH_3)_4](NO_3)_2$	0.0004	0.18
modified	$[Pt(NH_3)_4]Cl_2$	0.01	0.036
modified	$[Pt(NH_3)_4]Cl_2$	0.0004	0.051
modified	$[Rh(NH_3)_5Cl]Cl_2$	0.01	0.15
modified	$[Rh(NH_3)_5Cl]Cl_2$	0.0004	0.22
modified	$[Ir(NH_3)_5Cl]Cl_2$	0.01	0.039
modified	$[Ir(NH_3)_5Cl]Cl_2$	0.0004	0.055

[a]Calculated on the basis of XPS data using the Kerkof model.[12]

The pretreated Sibunit was immersed in a 0.01 or 0.0004 M aqueous solution of $[Pd(NH_3)_4](NO_3)_2$, $[Pt(NH_3)_4]Cl_2$, $[Rh(NH_3)_5Cl]Cl_2$ or $[Ir(NH_3)_5Cl]Cl_2$ and kept under stirring for 6 h at room temperature. Preliminary experiments indicated that an equilibrium concentration of the adsorbed complexes is achieved in less than 3 h. The excess of the complex was washed out thoroughly, and the samples were dried at 120 °C overnight.

X-ray photoelectron spectra were measured on an XSAM-800 spectrometer (Kratos) using Al K$\alpha_{1,2}$ radiation for spectra excitation. Atomic ratios were calculated from the integral intensities of XPS peaks using Scofield's photoionization cross-sections for Al K$\alpha_{1,2}$ excitation.[6] The accuracy of measurements was checked using the initial complexes and was estimated as ±15%. The binding energies of peaks were corrected to account of sample charging by referencing to the C 1*s* peak at 285.0 eV.

Figure 1 shows the XPS spectra of the samples containing Pt and Pd species. Obviously, the technique applied to the adsorp-

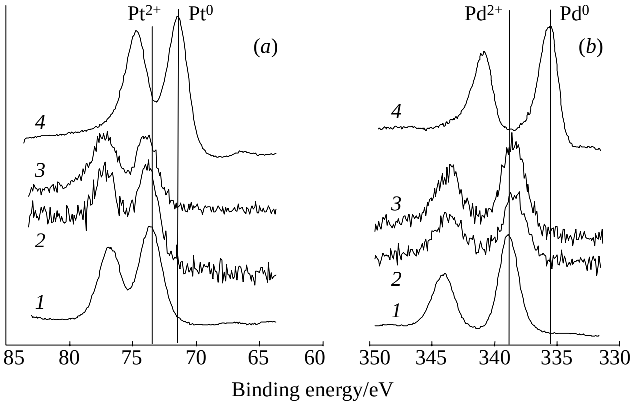


Figure 1 XPS spectra of (*a*) Pt 4*f* and (*b*) Pd 4*f* in complexes supported on the modified Sibunit surface: (*1*) initial complex; (*2*) surface complex deposited from a 0.0004 M solution; (*3*) surface complex deposited from a 0.01 M solution; (*4*) metal foil.

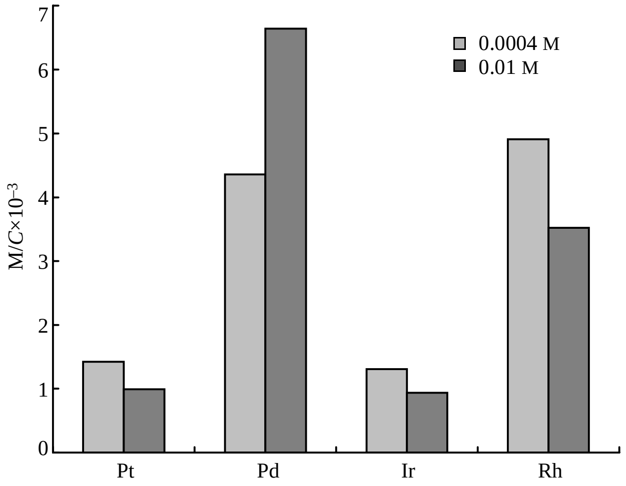


Figure 2 Effect of the nature of the complexed metal and its concentration in solution on the metal concentration at the Sibunit surface.

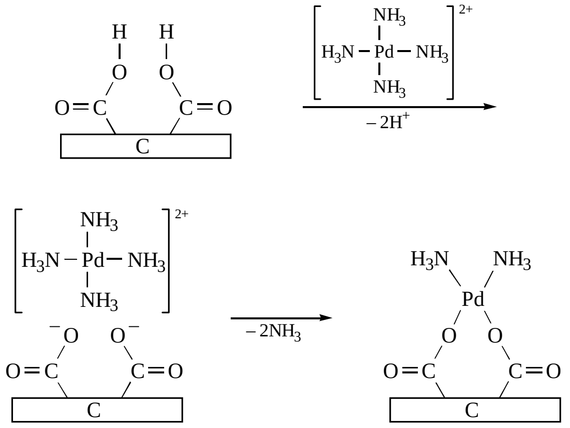
tion of cationic complexes allows us to avoid the formation of metal particles during ion exchange. Similar results were obtained for the Ir- and Rh-containing samples.

The dependence of the surface metal concentration on the nature and concentration of the metal in solution is depicted in Figure 2. The ion-exchange capacity of the Sibunit calculated on the basis of these data is given in Table 1. The exchange capacity of the modified Sibunit surface appears to be a function of the nature of the complex rather than its solution concentration. Modified Sibunit shows a maximum capacity towards Pd and Rh, while the capacity towards Pt and Ir is markedly lower.

As the XPS data indicate, the nitrogen-to-metal (N/M) atomic ratio decreases with increasing surface concentration of the metal complex (Figure 3). For the samples containing low concentrations of Pt and Ir, the N/M ratio remains practically the same as in the initial complexes. The positions of the Pt 4*f* and Ir 4*f* peaks also remain almost unchanged. However, a further increase in the concentration of the adsorbed complex is accompanied by a significant decrease in the N/M ratio. This effect is well pronounced for Pd- and Rh-containing complexes. A shift of the corresponding XPS peaks is also observed [Figure 1(*b*)], which can indicate a change in the structure of the complex ion on the Sibunit surface (*e.g.*, due to a change in the coordination number of the metal ion[7]).

The following tentative interpretation may be proposed in explanation of the behaviour of the noble metal complexes on the surface of the carbon support. According to the mechanism proposed by Morikawa,[8] oxidation of the carbon surface results in the formation of carboxyl groups. Protons of the carboxyl groups can be exchanged with metal ions.

In accordance with the Morikawa mechanism, the inner sphere of the complex remains intact and the complex is bound to the surface groups only by electrostatic forces. However, our data indicate that, in part, the ligands can be substituted, presumably with oxygen atoms of carboxyl groups. This leads probably to the formation of M–O–C bonds.



The final structure of the adsorbed complex seems to be a function of the stability constants of the corresponding complexes. According to Grinberg *et al.*,[9,10] the overall stability constant for $[Pt(NH_3)_4]^{2+}$ is about five orders of magnitude higher than that for $[Pd(NH_3)_4]^{2+}$. This effect is evidently caused by the so-called ‘lanthanide contraction’.[11] Presumably, the stability constants for $[Ir(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Cl]^{2+}$ change in the same direction (the corresponding data could not be found in the literature):

$$[Pt(NH_3)_4]^{2+} \approx [Ir(NH_3)_5Cl]^{2+} >> [Pd(NH_3)_4]^{2+} \approx [Rh(NH_3)_5Cl]^{2+}$$

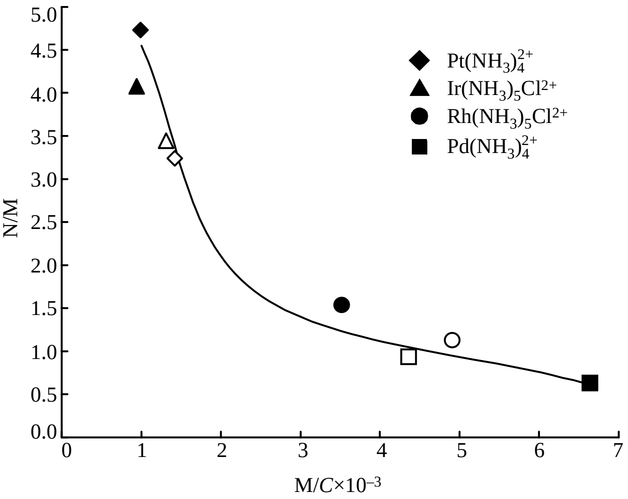


Figure 3 Dependence of the N/M ratio in the supported complexes on the surface metal concentration. Empty and filled symbols correspond to the samples prepared by ion exchange from 0.0004 M and 0.01 M solutions, respectively.

Since Pt and Ir complexes are significantly more stable than Rh and Pd complexes, the elimination of NH_3 ligands and the formation of –O–M bonds in the course of the ion exchange occurs more easily for the Pd and Rh complexes. This results in their stronger bonding to the support surface and, in turn, in a higher concentration of the supported metal.

Thus, the oxidative modification of the Sibunit surface followed by ion exchange with noble metal complexes makes it possible to avoid reduction of the adsorbed metal ions and facilitates the control of the adsorption process. The surface concentration of adsorbed metal ions and the structure of the metal complexes appear to be a function of the stability constants of the corresponding inner-sphere complexes.

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