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XPS Evidence for the Formation of Ni(II) Complexes on Treated Activated Carbon

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Abstract

X-ray photoelectron spectroscopy (XPS) was applied to a solid-state investigation on adsorbed systems obtained by contacting different samples of an activated carbon (Chemviron Filtrasorb 400) with solutions containing (a) 1,10-phenanthroline (phen); (b) $NiCl_2 \cdot 6H_2O$. (c) Ni^{2+} ions and phen in a 1:3 molar ratio.

XPS results on these systems are discussed with particular regard to the chemical state of the ligand (interaction of functional groups with the substrate) and of the metal ions on carbon (assessment of Ni oxidation state; detection of Ni complexes on carbon and information on their stoichiometries and structures). Various effects of successive chemical treatments on the above reported carbon species were also revealed by XPS, such as:

(i) the formation of a 'carbon–ligand' system (activated carbon with ligand firmly present on it) after acid elution of the activated carbon treated with Ni–phen complexes in solution, and (ii) the adsorption of Ni^{2+} ions on this 'carbon–ligand' system, with fomation of Ni–phen complexes on carbon.

Introduction

Adsorption reactions in solid–liquid systems have often been proposed as methods for elimination and/or recovery of heavy metals from industrial waste waters.

Activated carbons are well-known supporting materials for the adsorption of heavy metals, present in complexed form, from their aqueous solutions. In previous papers [1–3] we verified for various organic and inorganic ligands and metals couples that the adsorption of metal ions on carbon is enhanced in the presence of ligand in solution. Some of the systems resulting from these adsorption experiments can be regenerated by elution with acids, which dissociate the metal complexes adsorbed on carbon with dissolution of the metal ions, while the ligand is fixed on the substrate. This 'carbon–ligand' species may enter successive adsorption and regeneration cycles, similar to an ion-exchange material towards the metal ion in solution [3] and it is of interest for practical applications.

In the present paper we collect the result of a preliminary application of the XPS technique to these carbon systems.

XPS is a surface-sensitive technique, being able to give information on the first atomic layers to ~100 Å of a solid surface, and it is a powerful and unique tool in the study of formation, composition and structural identification of the chemical species existing in adsorbed systems.

The system chosen here for a first XPS approach was suggested in part by our previous adsorption experiments: among various metal–ligand couples which we investigated with different techniques, nickel–phenanthroline showed high (although not unique) values of adsorption capacity on carbon, and a relatively easier recovery of metal ions by acid elution of carbon [3], a property of fundamental importance for practical applications of this system. Moreover, Ni(II) high-spin complexes show some interesting XPS features: Ni $2p_{3/2}$ and $2p_{1/2}$ principal ionization lines are generally accompanied by additional peaks on the high binding energy (b.e.) side. These peaks, the nature of which is still under discussion, are referred to as 'shake-up satellites' lines. The position in the b.e. energy scale and the shape of these peaks are influenced, to a various extent, by the nature of the ligand and by stoichiometry and stereochemistry of the metal–ligand complexes, thus furnishing a powerful aid to structural studies of these species.

The application of XPS in solid state to the 'activated carbon–Ni–phen' model system, may help to

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TABLE I. Binding Energies (eV) and Full-width at Half Maximum (FWHM) Values (eV) for Electronic Levels of the Compounds. ΔE is the separation between the b.e. value at the shake-up satellite structures maxima and the b.e. value at Ni2$p_{3/2}$ maximum; sh is a shoulder on the high b.e. side of C 1s peak.

	C 1s	N 1s FWHM	Ni 2$p_{3/2}$ FWHM	Cl 2p FWHM	ΔE
(1) 1,10-phenanthroline	285.0	399.1(1.9)	–	–	
(2) [Ni(phen)$_2$Cl$_2$]	285.0	399.4(2.1)	855.4(2.5)	199.5(3.3)	5.6
(3) [Ni(phen)$_3$]Cl$_2$	285.0	399.5(1.8)	855.8(2.4)	197.2(3.2)	6.0
(4) NiCl$_2$·6H$_2$O	285.0	–	856.8(2.7)	199.4(3.1)	5.4 8.5
(5) Activated carbon	284.8 + sh	–	–	–	–
(6) 1,10-phen·HCl on activated carbon	284.8 + sh	399.0(2.5)	–	197.4(3.2)	–
(7) NiCl$_2$·6H$_2$O on activated carbon	284.8 + sh	–	856.5(2.8)	199.7(3.5)	5.4 8.5
(8) [Ni(phen)$_3$]Cl$_2$ on activated carbon	284.8 + sh	399.3(3.1)	855.6(2.8)	197.2 200.2 (6.0)	6.0
(9) Compound (8) treated with HCl	284.8 + sh	399.2(3.1)	–	197.7 200.3 (7.0)	–
(10) Compound (9) treated with NiCl$_2$·6H$_2$O	284.8 + sh	399.5(2.0)	855.5(2.5)	197.5 200.3 (6.5)	6.0

assess different mechanisms of interaction between the metal ions in solution and the surface of carbon, when the nature of the solution and/or treatments of the substrate are varied.

Experimental

The activated carbon used in this study was powdered Filtrasorb 400 Chemviron, washed with hot distilled water and then with 37% HCl for 3 h, successively washed with distilled water to neutrality and dried at 120 °C for 8 h.

Solutions were prepared with reagent grade chemicals: 1,10-phenanthroline·HCl monohydrate was a Merck product and NiCl$_2$·6H$_2$O was supplied by Riedel-De Haen AG. [Ni(phen)$_3$]Cl$_2$ and [Ni(phen)$_2$Cl$_2$] were prepared and purified according to literature procedures [4].

Sample (6) was obtained by contacting 1 g of activated carbon with 100 ml of a solution containing 8 g/l of 1,10-phenanthroline·HCl; the sample was filtered, washed with distilled H$_2$O to neutrality and dried at 120 °C for 8 h.

Sample (7) was prepared by contacting 1 g of activated carbon with an acid (pH $\simeq$ 5) solution of NiCl$_2$·6H$_2$O, containing 1 g/l of Ni^{2+}; and subsequently treated as sample (6).

Sample (8) was obtained by contacting 1 g of activated carbon with 100 ml of a solution containing 1 g/l of Ni^{2+} and phen in a 1:3 molar ratio with the metal ions, for 24 h (pH = 5.8). Subsequent treatment was as before.

Sample (9) was obtained by contacting 1 g of sample (8) with 10 ml of HCl (1 N) for 24 h, washing with water to neutrality and drying at 120 °C for 8 h.

Sample (10) was obtained by contacting 1 g of sample (9) with a moderately acid solution of NiCl$_2$·6H$_2$O containing 1 g/l of metal ions and then filtering, washing and drying as before.

The XPS spectra were run on a VG-ESCA 3 photoelectron spectrometer, employing Al-K$_\alpha$ radiation (1486.6 eV).

Radiation damage was negligible during the spectra acquisition.

Uncertainty in the reported b.e. values corresponds to an experimental error of ±0.2 eV.

The XPS spectra of Ni 2p in compounds (8), (9) and (10) were accumulated with a Laben 8004 multichannel, to improve the signal-to-background ratio.

Results and Discussion

The XPS experimental results obtained for reported carbon systems are collected in Table I. XPS measurements on samples (1) to (4) are reported in Table I for comparison with related adsorbed species.

Activated Carbon

The XPS spectrum of pure activated carbon was practically free of detectable ionization lines, other than the main C and O photoelectron peaks. The O 1s peak is largely due, under our experimental conditions, to contaminant species, mainly polyphenolic ethers from the diffusion pump oil.

The C 1s peak shows a strong maximum centred at a b.e. value of 284.8 eV, and a much weaker structure extending up to ~293 eV: this structure shows a maximum at 289.3 eV. The existence of such an extended structure confirms the presence of numerous different organic and inorganic carbon functions on the active surface. In particular, the maximum at 289.3 eV may be ascribed to the presence of carboxylic and ester functions [5, 6].

Our results are in agreement with previous reports [7–13] obtained with different techniques, where some authors ascribed some activated carbon reactions specifically to the presence of some of these functionalities on the surface of the substrate.

Activated Carbon Loaded with phen Ligand (sample (6) in Table I)

The C 1s peak of sample (6) shows only minor differences in position, shape and relative intensity of peak maximum and peak structure with the C 1s line already discussed for pure activated carbon. The N 1s peak falls at 399.0 eV, a value which is identical, within the experimental error (±0.2 eV), to that we reported in Table I for N 1s in the case of free phen (399.1 eV). This result may be ascribed either to a purely physical interaction between the two species (on the surface and/or within the micropore cavities of activated carbon), or to a more specific interaction through the extended systems of π orbitals of the two species. In either case, the nitrogen ligand functions of phen show no σ-interaction with carbon, therefore remaining available to act as donors.

Activated Carbon Loaded with $NiCl_2 \cdot 6H_2O$ (sample (7) in Table I)

Sample (7) was obtained experimentally by contacting a sample of activated carbon with a $NiCl_2 \cdot 6H_2O$ solution containing 1 g/l of metal ions (see Experimental for more details).

In previous papers [1–3] we discussed the adsorptive capacity of Ni^{2+} ions on activated carbon in the absence and presence of ligand species. The XPS analysis of sample (6) was performed mainly to investigate the nature of the interactions of the metal ions and carbon and to relate the coordinative situation of Ni on carbon in this sample and in the more complex cases represented by sample (8) and (10), where the adsorption experiments were conducted on $NiCl_2$ in the presence of phen in solution and, respectively, on $NiCl_2$ in contact with a previously treated carbon substrate.

The low intensity of the XPS peaks attributable to the most intense ionization lines of Ni and Cl directly confirms that, in our experimental conditions, activated carbon adsorbed only a small quantity of $NiCl_2$.

The C 1s line was found to be constant in peak maximum position and in overall shape when compared to pure activated carbon. The Ni $2p_{3/2}$ b.e. value (856.5 eV) and the Cl 2p b.e. value (199.7 eV) are quite close to values given in Table I for pure $NiCl_2 \cdot 6H_2O$ (856.8 and 199.4 eV respectively).

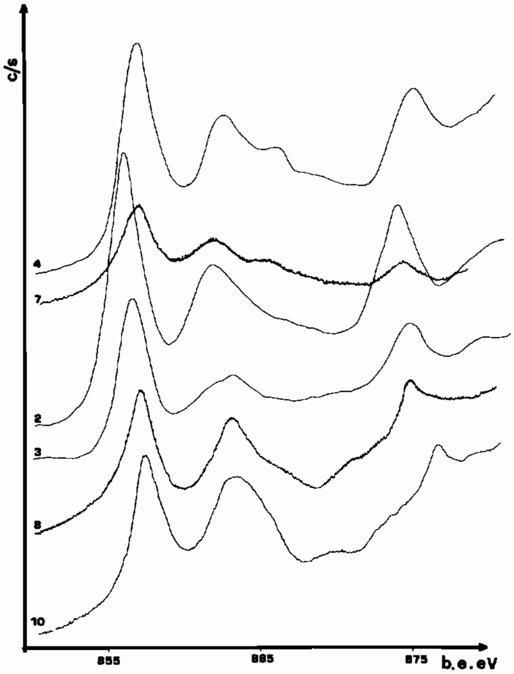

Fig. 1. Ni $2p_{3/2,1/2}$ XPS spectra for samples (4), (7), (2), (3), (8) and (10).

The b.e. values collected for sample (7) show that interaction of the $NiCl_2$ with the carbon substrate is weak. We can however proceed further in the analysis of sample (7) and examine the structures accompanying Ni 2p main ionization peaks 'shake-up satellites') reported in Fig. 1. The shape, intensity and ΔE values (these last representing the energy separation between b.e. values at satellites maxima and at parent peak) of the Ni 2p shake-up satellites in this sample are in good agreement with the case of pure $NiCl_2 \cdot 6H_2O$.

The chemical nature of the complex adsorbed is therefore confirmed to be $NiCl_2$.

In conclusion, the small quantity of $NiCl_2 \cdot 6H_2O$ adsorbed on our samples of activated carbon is present chemically unmodified on the surface of carbon samples.

The Activated Carbon–Ni–phen Systems (samples (8), (9), (10))

In a recent paper [3] on the adsorption of various metal-ligand couples on activated carbon we discussed the results of applying cycles of adsorption and elution on the Ni–phen system, either in batch and in a laboratory scale plant, typically consisting of a series of 4 columns containing each 100 g of activated carbon, working continuously with 3 adsorbing columns and a single column being regenerated at a time. We found that such a system can completely remove the metal content from a water solution containing 100 mg/l of Ni^{2+} [3].

The next three samples (8), (9) and (10) are strictly related (see Experimental) and simulate different steps of a cycle of Ni extraction (sample 10) and elution (sample 9), which can be renewed continuously [3] aftcr a preliminary phasc of adsorption on carbon of metal complexes from solution (sample 8). Here we examine them in the same sequence in which they were prepared: (8) → (9) → (10).

Activated carbon treated with a solution containing Ni^{2+} and phen in a 1:3 molar ratio (sample (8) in Table I)

As reported in the Introduction, adsorption of metal ions on activated carbon is generally influenced by the presence of ligand/s in solution [1–3]. In this section we are particularly interested in relating XPS results on Ni adsorption in the absence (sample 7) and presence (sample 8) of phen in solution, examining the structural characteristics of the species present on carbon, as revealed by XPS.

The analysis of photoelectron peaks for sample (8) shows that the C 1s peak is similar, in the shape and b.e. value, to pure activated carbon.

The Ni $2p_{3/2}$ b.e. falls at 855.6 eV. This value is different from the Ni $2p_{3/2}$ b.e. value for sample (7); it lies between the values that we obtained for $[Ni(phen)_2Cl_2]$ (855.4 eV, sample (2) in the Table I) and for $[Ni(phen)_3]Cl_2$ complexes (855.8 eV, sample (3)), although the difference is about of the same order as the experimental uncertainty (±0.2 eV).

As in the case of sample (7), more information comes from the analysis of the Ni 2p shake-up satellites. An evident component in the high b.e. side of the Ni $2p_{3/2}$ peak strongly suggests, by analogy with previous XPS literature findings [14–16], that an octahedral coordination is present for the complex on carbon. Moreover, the ΔE values, shape and intensity of these satellites are close to (even though not strictly coincident with) the values already reported in the literature for $[NiN_6]$ chromophores [14].

These results suggest that the $[Ni(phen)_3]^{2+}$ complex, which is the predominant species present in an aqueous solution of Ni^{2+} and phen (in a 1/3 molar ratio), is adsorbed from its aqueous solution on activated carbon. There is however some evidence for the presence of other octahedral species on carbon (among which, presumably, $[Ni(phen)_2Cl_2]$) which are also present in equilibrium in the solution considered.

The N 1s peak presents a full width at half maximum (FWHM) value of 3.1 eV, larger than in the case of sample (6) (2.5 eV), where the N 1s signal was due to 'free' phen adsorbed on carbon. The centre of gravity of this signal falls at 399.3 eV, a value which is about half-way between reported N 1s b.e.s for phen on carbon (399.0 eV), and for $[Ni(phen)_2Cl_2]$ and $[Ni(phen)_3]Cl_2$ (399.4 eV, respectively 399.5 eV). N 1s data suggest the presence of some uncomplexed phen on carbon, under our experimental conditions.

The Cl 2p FWHM value (6.0 eV) unequivocally establishes the existence of at least two different species for chlorine, with b.e. values tentatively found at 197.2 eV (*i.e.* in the region typical for Cl^- counterions in $[Ni(phen)_3]Cl_2$) and 200.2 eV (*i.e.* in the region of coordinated Cl ligands, as in $[Ni(phen)_2Cl_2]$ complex). These results suggest the possible occurrence of further chlorinated species on the surface of carbon.

'Treated' activated carbon: the 'carbon–ligand' species (sample (9) in Table I)

Elution with HCl at pH = 0 of sample (8) gives rise to sample (9) (see Experimental).

The analysis of XPS data for this system reveals the lack of any signal attributable to Ni 2p ionizations and that the N 1s peak falls at 399.2 eV, a value practically coincident, within experimental error, with the value we obtained for N 1s in 'free' phen (399.1 eV). These data support the presence of uncomplexed phen on activated carbon, thus confirming that acid elution conducted on previously adsorbed Ni complexes generates 'functionalized' activated carbon.

Adsorption of Ni^{2+} ions on 'treated' activated carbon (sample (10) in Table I)

Sample (10) was obtained experimentally by treating 1 g of sample (9) with a solution containing $NiCl_2$ (see Experimental for details).

The ability of 'treated' activated carbon in extracting Ni^{2+} ions from aqueous solutions has been experimentally tested with positive results [3]. XPS data should afford structural information on the species present on carbon and a more thorough characterization of the mechanism of Ni adsorption on the functionalized substrate.

The b.e. value for Ni $2p_{3/2}$ falls at 855.5 eV, a value which is quite different from that reported for $NiCl_2$ on carbon (856.5 eV), but falling in the restricted range of values reported above for $[Ni(phen)_2Cl_2]$ and $[Ni(phen)_3]Cl_2$ (855.4 and 855.8 eV, respectively).

The b.e. value of the N 1s peak (which is due, in our experimental conditions, only to phen *already* present on carbon, before the treatment with $NiCl_2$) is 399.5 eV. coincident with N 1s b.e. value reported for $[Ni(phen)_3]Cl_2$ and quite close to the N 1s b.e. values in $[Ni(phen)_2Cl_2]$ and in sample (8).

Relevant data is presented by the N 1s FWHM value in sample (10): 2.0 eV, against a value of 3.1 eV for the same peak in the parent system (9), indicating more homogeneous bond situations of N atoms in the former case.

Taken as a whole these data clearly indicate that, under our experimental conditions, phen N donor functions are involved in coordinative bonds with Ni.

The nature of the Ni coordinative bonds is assessed by examining Ni 2p satellite lines; their position, shape and intensity indicate the formation of octahedral complexes on carbon.

Further details emerge from the analysis of the ratio of peak areas for Ni $2p_{3/2}$ and N 1s in sample (8) and (10). For sample (10) this ratio is higher by a factor of ~2 than for sample (8). Presumably, this indicates that different stoichiometries for $[Ni(phen)_x]^{2+}$ complexes on carbon exist in the two samples. Consequently, if metal ion adsorption is performed starting from 'treated' carbon and a solution of $NiCl_2$, we should observe the presence of $[Ni(phen)_x]^{2+}$ complexes with $x < 3$ to a greater extent than when the adsorption starts from 'pure' activated carbon and a solution containing Ni^{2+} and phen in a 1:3 molar ratio.

A possible explanation of this behaviour may lie in a different possibility for Ni^{2+} ions of coordinating phen molecules in solution (sample 10)) with respect to the case in which phen ligands are distributed on the surface of activated carbon (sample (8)).

Conclusion

The XPS technique, which offers unique sampling and interpretative possibilities on adsorbed systems, has afforded various experimental information on the chemical composition and mechanism of adsorption of carbon species.

The first XPS result is that interaction of activated carbon with phen ligands does not involve to a first approximation nitrogen ligand functions (via σ-bonds) which can subsequently act as donor functions towards the metal ions; this interaction may be physical in nature or it may involve the π-orbital systems of the two species.

A particularly interesting result obtained with the application of XPS is that the activated carbon interacts with a solution of Ni^{2+} and phen in a 1:3 molar ratio with formation of octahedral complexes with phen ligands ($[Ni(phen)_3]Cl_2$ and $[Ni(phen)_2Cl_2]$ are, presumably the species predominantly present on carbon).

Acid elution of the activated carbon treated with Ni^{2+} complexes in solution generates 'treated' activated carbon, with uncomplexed ligand firmly adsorbed. This carbon system can subsequently extract Ni^{2+} ions from aqueous solution, with formation of chemical bonds between the species, and hence complex species on carbon.

Evidence for the formation, on carbon, of different $[Ni(phen)_x]^{2+}$ complexes with various stoichiometries, when the adsorption conditions are varied, has been revealed by semi-quantitative XPS data.

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