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EXAFS STUDIES WITH SYNCHROTRON RADIATION OF POLYSTYRENE-RUTHENIUM CATALYST

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ABSTRACT

The local structure of the metal atom surroundings in polystyrene-ruthenium complexes (PSt-Ru) has been studied by EXAFS (Extended X-ray Absorption Fine Structure) at Frascati Laboratories by using the "Wiggler" beam line of the ADONE storage ring. In such study the EXAFS at the Ru-K-edge (22.118 keV) has been measured for both metallic Ru and PSt-Ru. Numerical elaboration of the data observed allows the determination of the ruthenium-carbon distance ($d=2.05 \text{ \AA}$) and the number of carbon atoms coordinated to the metal (coordination number $C_oN_o=6$) in PSt-Ru.

INTRODUCTION

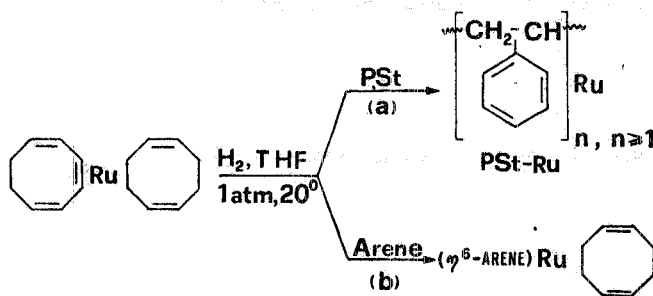
Extended X-ray Absorption Fine Structure (EXAFS)⁽¹⁾ is a powerful tool for structural studies of noncrystalline materials. A very interesting application is offered by the structural analysis of homogeneous metal complexes supported on polymers, for which is very difficult to obtain structural information⁽²⁾.

Polymer-metal complexes are prepared by the reaction of a transition metal complex and an insoluble polymeric support and can act as heterogenized catalysts in several reactions of industrial interest⁽³⁾. Moreover these systems can display in some cases exceptional catalytic properties with respect to the unsupported monomeric analogs. A remarkable example is offered by polystyrene-ruthenium complexes (PSt-Ru) prepared by reacting Ru(COT)(COD)(COT = η^6 -cyclooct-1, 3, 5-triene; COD = η^4 -cycloocta-1, 5-diene) with polystyrene (PSt) under hydrogen atmosphere ($p_{H_2}=1$ atm) at 20°C in tetrahydrofuran (scheme I, step a)⁽⁷⁾. Using monomeric aromatic derivatives the same reaction gives arene-ruthenium complexes of the type Ru(η^6 -arene) (COD) (scheme I, step b)⁽⁴⁻⁵⁾.

The PSt-Ru complexes show catalytic activity in the hydrogenation, under relatively mild conditions ($p_{H_2}=50$ atm, $T=20-80^\circ\text{C}$), of a wide range of unsaturated substrate such as olefins, aromatic hydrocarbons, ketones, oximes, nitroderivatives, whereas the monomeric complexes, acting in solution, is only active for olefins hydrogenation⁽⁴⁻⁶⁾.

Elemental analysis, IR and mass spectra indicate that the PSt-Ru complexes do not contain the cycloolefine ligands initially present in the Ru(COT)(COD) compound, which are probably displaced by the phenyl rings of the polystyrene.

In order to obtain more detailed information on the metal environments in these compounds and particularly on the presence of arene-ruthenium bonds, an EXAFS analysis was effected on the PSt-Ru complex having a phenyl/ruthenium molar ratio $(n)=2$.



EXPERIMENTAL

The EXAFS measurements have been performed at the Wiggler Facility of the National Laboratories in Frascati. The Synchrotron Radiation was generated by a transverse Wiggler magnet installed on the ADONE storage ring⁽⁷⁾. The X-ray beam was monochromatized by a channel-cut Silicon (111) single crystal. The total energy resolution of the apparatus was about 4.5 eV at the K-edge of Ru, mainly due to the intrinsic resolution of the crystal and the angular vertical divergence of the beam. The step width of the rotating table was about 4.3 eV, corresponding to rotation steps of 0.001 degree. The detection system consisted in two ionization chambers filled with Argon. The whole apparatus was remotely controlled by means of a PDP 11/40 computer.

In order to optimize the signal to noise ratio a value of $\mu x=2$ was chosen for the sample thickness PSt-Ru.

This complex was prepared as described in the literature⁽⁴⁾ from atactic polystyrene ($\bar{M}_v=86,000$) and from Ru(COT)(COD)⁽⁸⁾. Ru metal, Fluka product, with purity larger than 99.9% was used. The samples of PSt-Ru and Ru-metal consisted of fine powders enclosed between two adhesive Kapton tapes in order to protect them from moisture and to form an uniform very thin film.

RESULTS

The K-edge X-ray absorption spectra (XAS) of metallic ruthenium and PSt-Ru are reported in Figs. 1 and 2, respectively.

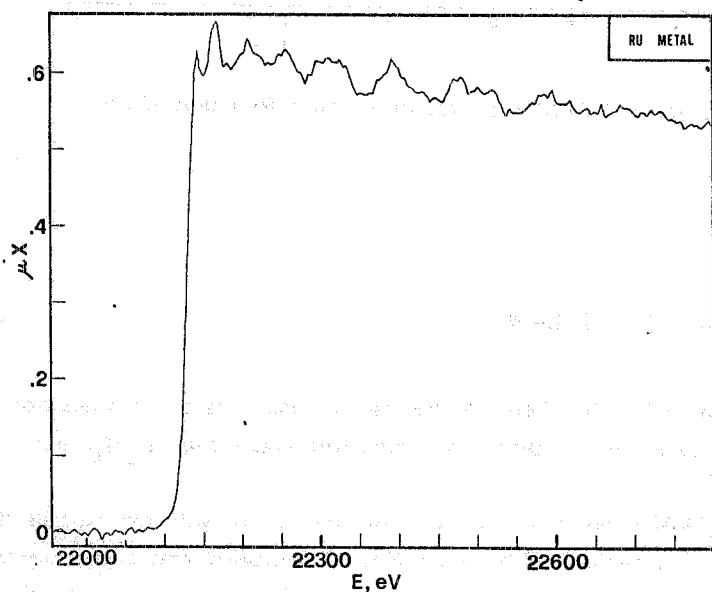


FIG. 1 - K-edge X-ray absorption spectrum (XAS) of metallic ruthenium.

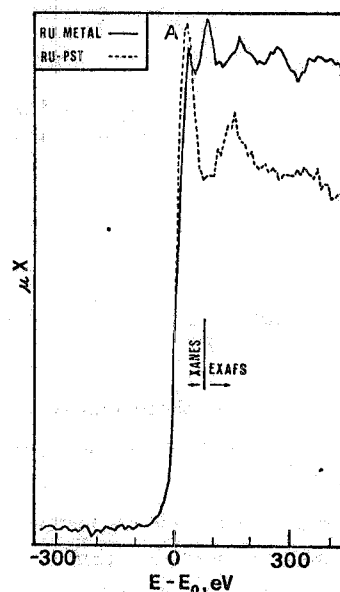


FIG. 2 - K-edge X-ray absorption spectrum (XAS) of the polystyrene-ruthenium complex with a phenyl group to ruthenium ratio (n) equal to 2.

Two energy regions must be distinguished, the so called "XANES region", for $E-E_0$ over ~ 40 eV, and the "EXAFS region", for $E-E_0$ below ~ 40 eV^(9,10).

The XANES features are due to multiple scattering resonances and therefore their intensities and energy positions are determined both by the relative positions of many atoms around the absorbing one and by the type of atoms (Ru or C). The different XANES features in the spectra of Ru-metal and PSt-Ru show immediately that both type and geometrical coordination of atoms around the Ru-atom are different in the two systems. The strong multiple scattering resonances A in the PSt-sample (Fig. 2) should be due to C atoms in the first shell coordination which have their backscattering amplitude at low kinetic energy of the photoelectron. This is confirmed by the EXAFS analysis. Indeed the Fourier Transform indicates (Fig. 3a) that the Ru-Ru distance is about 2.3 Å, thus the peak at 1.34 Å (Fig. 3b) in PSt-Ru should be assigned to Ru-C distance which is expected to be shorter than Ru-Ru distance⁽¹¹⁾. The second peak at 2.56 Å in the spectrum of the complex (Fig. 3b) can then be tentatively assigned to the Ru-atoms in the second coordination shell. Ru-Ru and Ru-C distances have been determined on the basis of the best fitting of EXAFS oscillations. The EXAFS of the first coordination shell is given by the equation:

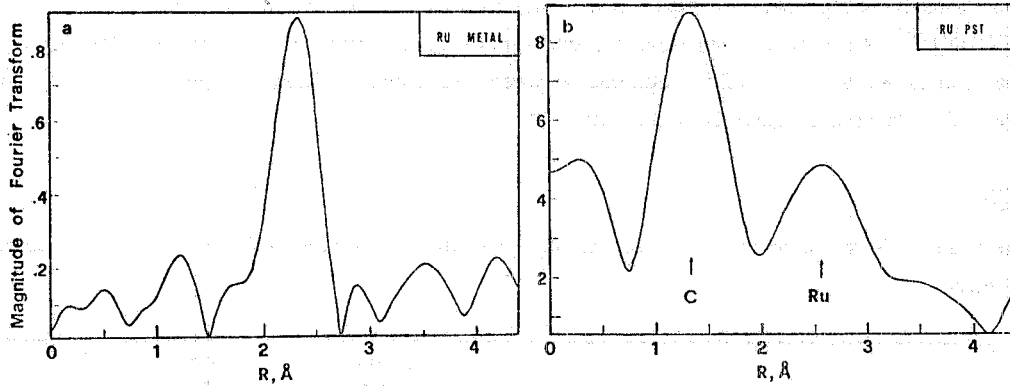


FIG. 3 - Fourier Transform of EXAFS spectra for metallic Ru (curve a) and PSt-Ru (curve b).

$$k \cdot \chi(k) = \frac{N}{R^2} e^{-2k^2\sigma^2} A(k) \sin(2kR + \phi_a(k) + \phi_b(k) - \pi) \quad (1)$$

where k is the photoelectron wavevector, σ^2 is the Debye-Waller factor, and N is the coordination number. Metallic ruthenium was used as model compound to check the calculated phase shift ($\phi_a + \phi_b$) and amplitude ($A(k)$)⁽¹²⁾.

Fig. 4 shows the comparison of the EXAFS spectrum calculated by equation (1) with the experimental back transform of the main peak in the Fourier Transform of Ru from Fig. 3a, indicated that a good agreement is obtained (Fig. 4) with Ru-Ru mean distance of 2.68 Å, coordination number (C.N.) of 12 and $\sigma^2 = 0.0037 \text{ Å}^2$. This good agreement allows us to use the amplitude $A(k)$ and the central atom phase shift ϕ_a of Ru for unknown

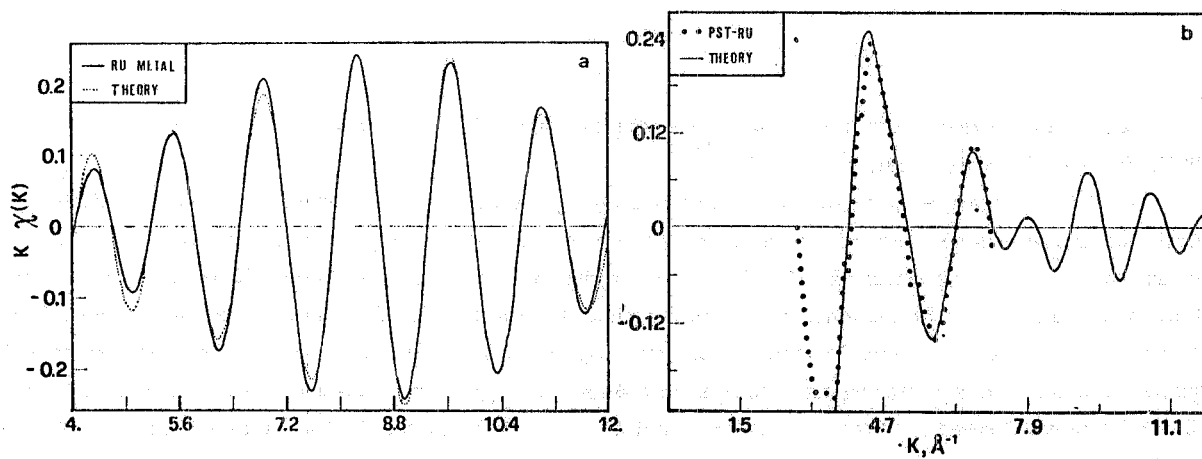


FIG. 4 - Calculated and experimental EXAFS for (a) metallic Ru and (b) PSt-Ru complex.

compounds. The Ru-C distance of PSt-Ru has been obtained by fitting the experimental EXAFS spectrum with two shells the former of Carbon atoms and the latter of Ru. For the first shell we have used the ϕ_a of Ru so checked and ϕ_b taken from ref. (12). In the fitting procedure a ruthenium-carbon distance Ru-C of $2.05 \pm 0.05 \text{ \AA}$ and C.N. of 6 ± 1 was obtained with a Ru-Ru distance of $2.88 \pm 0.1 \text{ \AA}$.

The number of coordinated Ru atoms cannot be accurately determined because of the noise in the spectrum, the best fit giving a value of C.N. = 2 ± 2 .

DISCUSSION

These results are consistent with the presence of Ru-atoms complexed to a single phenyl ring of the polystyrene side chains, excluding bis-arene systems. Indeed the Ru-C distance determined in PSt-Ru is in good agreement with the typical Ru-C distances in homogenous monomeric Ru-arene complexes⁽¹³⁾. Moreover, accepting the hypothesis of Ru atoms in the second shell, the Ru-Ru distance found (2.88 \AA) is similar to that found in small (C.N.=6) ruthenium clusters containing bonded arenes⁽¹⁴⁾ and appreciably different from that of metallic Ru (2.68 \AA)⁽¹¹⁾.

Even if these results are to be considered as preliminary, they allow to hypothesize for PSt-Ru complexes a structure in which small Ru clusters are attached to polystyrene by complexation of Ru-atoms to a single phenyl ring. This is consistent with the variable stoichiometry of these systems, obtained starting with different PSt-Ru (COT) (COD) weight ratio, and with IR spectra indicating the presence of noncoordinated phenyl groups⁽⁴⁾.

Moreover the presence of clusters and coordinatively unsaturated Ru-atoms allows to explain the better catalytic properties of PSt-Ru with respect to Ru (η^6 -arene (COD) complexes⁽⁴⁻⁶⁾.

Finally, these findings confirm that EXAFS is a very useful technique for understanding the structure of heterogeneous catalysts obtained by attachment of transition metal complexes to polymeric ligands.

Further studies in progress on complexes with different phenyl/Ru ratio before and after catalysis as well as on model compounds, such as the 1,3-diphenylpropane -Ru complex⁽⁴⁾, will be reported in future papers.

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