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**EXAFS STRUCTURAL STUDIES OF
AROMATIC POLYMERS/RUTHENIUM CATALYSTS**

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The use of polystyrene as ligand to prepare macromolecular catalysts containing transition metals is made attractive by the easy accessibility of the polymer and the possibility of introducing required modifications.

New polystyrene/ruthenium complexes have been prepared and their catalytic activity has been studied^(1,2). These complexes have been obtained as amorphous solids, insoluble in the common chemical solvents, according to scheme of Fig. 1 (Ar = -C₆H₅). They are active in the hydrogenation of a wide range of unsaturated substrates as olefins, aromatic hydrocarbons, ketones, nitriles, nitroaromatic compounds and oximes⁽³⁾.

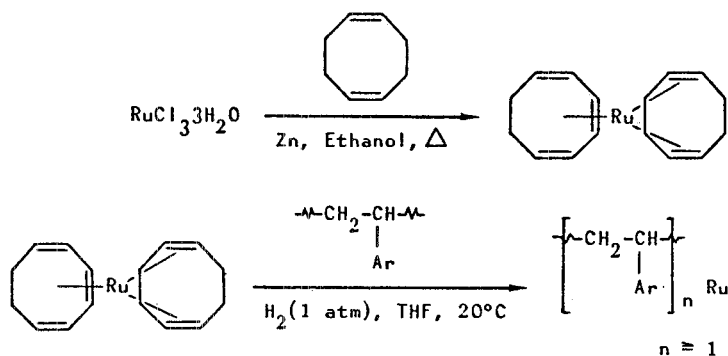


Fig. 1

To thoroughly understand the catalytic properties of these complexes one needs to know how the metal atoms are bonded to the polymeric support. For this reason we have carried out EXAFS measurements on the following compounds:

- a) Samples with polystyrene/ruthenium molar ratio $n=1$ and $n=2$;
- b) Polystyrene/ruthenium samples recovered from catalytic runs;
- c) Samples containing poly-1-vinylnaphtalene as macromolecular arene ligand (Fig. 1, $Ar=C_{10}H_7$).

The measurements have been carried out at the synchrotron radiation facility PWA at the Frascati National Laboratories, utilizing a Si(220) monochromator.

The EXAFS spectrum on the Ru K edge in a sample with a phenil/ruthenium molar ratio $n=1$ recovered from a catalytic run is shown in Fig.2a, together with its Fourier Transform $F(R)$, Fig. 2b.

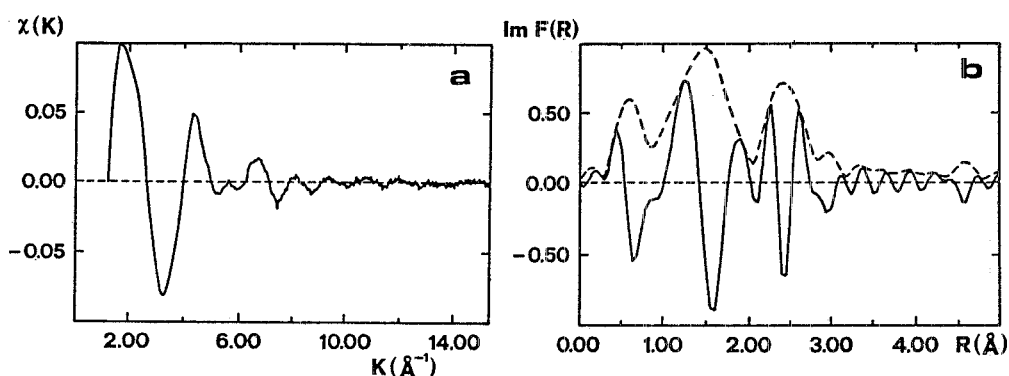


Fig. 2 - Experimental EXAFS spectrum of the Ru K edge in the polystyrene/ruthenium complex (a), and its Fourier transform (b).

The peak at about 1.6 \AA in Fig. 2b (dashed line) comes from the arene-Ru coordination, while the peak at about 2.4 \AA is due to the Ru-Ru bonds. The Ru-C distance of the Ru-arene bond is $2.05 \pm 0.02 \text{\AA}$; it has been determined by utilizing the phaseshift extracted from the model compound $\text{Ru}_3\text{CO}_{12}$. The Ru-C distance is in good agreement with the typical distance Ru-C detected in homogeneous monomeric Ru/arene complexes⁽⁴⁾. The distance Ru-Ru, determined by utilizing Ru metal as model compound, is $2.80 \pm 0.02 \text{\AA}$. It is 0.12 \AA greater than the Ru-Ru distance of the first coordination shell in Ru metal. This can be ascribed to a formation of small Ru clusters bonded to the aromatic rings of the polystyrene^(5,6).

The EXAFS spectrum of a sample recovered from two catalytic runs is almost identical to that of the same sample recovered from one catalytic run. This fact points out the good stability of these complexes after repeated hydrogenation processes.

The analysis of the EXAFS signal amplitude to determine the coordination number and Debye Waller factor around the metal atoms for the different samples, is in progress.

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