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EXAFS STRUCTURAL STUDIES OF AROMATIC POLYMERS/RUTHENIUM CATALYSTS

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Abstract - The coordination of ruthenium in polystyrene/ruthenium catalysts has been studied by EXAFS. Ru atoms result complexed to the phenyl rings and tend to group in small clusters. The extent of the clustering depends on the Ru concentration and grows when the compounds are utilized for the first catalytic run. Successive catalytic runs do not affect sensibly the coordination of Ru.

INTRODUCTION

In recent years the reactions between soluble complexes of transition metals and unsoluble polymeric materials have been widely investigated to prepare new compounds that can act as heterogeneous catalysts in reactions of industrial interest /1/. Between the examined supports polystyrene (PSt) appears as a suitable macromolecular ligand to prepare this kind of catalysts for its easy accessibility and for the possibility of introducing required modifications /2/. The characterization of the local structure of the supported metals is very important to understand the catalytic behaviour of these compounds. In this frame EXAFS has become an invaluable tool /3/; it is particularly useful when the metal atoms are highly and uniformly dispersed on the support. EXAFS allows to get information about both the structure of the metal clusters and the interaction between the metal atoms and the support /4/.

\[
\text{RuCl}_3\cdot 3\text{H}_2\text{O} \xrightarrow{\text{Zn, Ethanol, } \Delta} \text{RuC}_n\text{C}_m\text{H}_n
\]

Scheme 1
In previous papers /5,6/ the preparation of new polystyrene/ruthenium compounds, showing very interesting catalytic activity, has been reported. These compounds can be obtained as amorphous solids, unsoluble in the common solvents, by reaction between Ru(COT)(COD), (COT= cycloocta-1,3,5-triene, COD= cycloocta-1,5-diene), and PSt under hydrogen atmosphere (Scheme 1). They are active heterogeneous catalysts in the hydrogenation of a wide range of unsaturated compounds as olefins, aromatic hydrocarbons, ketones, nitriles and nitroderivatives /7/.

Preliminary EXAFS results on the structure of a sample with a phenyl/ruthenium molar ratio n=2 have been previously reported /8/. As a further structural investigation on this type of complexes we have carried out EXAFS measurements on samples containing a larger amount of ruthenium (phenyl/ruthenium molar ratio n=1), and on samples recovered from catalytic runs and re-used in hydrogenation reactions. The aim is to understand the influence of the metal loading on the catalyst structure and to know the life of the catalyst.

EXPERIMENTAL

Polystyrene/ruthenium compounds have been prepared as described in the literature /5/ from Ru(COT)(COD) and the corresponding atactic polymer. Metallic ruthenium, Fluka product, had a purity larger than 99.9%.

EXAFS has been measured at the edge Ru K by an X-ray absorption apparatus utilizing a Si(220) monochromator. The measurements have been carried out at the synchrotron radiation wiggler facility of the Frascati National Laboratories.

The samples consisted of fine powders placed in a suitable support and protected from moisture by adhesive kapton tapes.

RESULTS AND DISCUSSION

The Fourier Transforms (FT) of the EXAFS signals of the compounds PSt/Ru n=1, PSt/Ru n=2 and PSt/Ru n=2 subjected to a catalytic run are given in Fig. 1.

Preliminary EXAFS measurements on the PSt/Ru n=2 compound revealed the presence of Ru atoms complexed to single phenyl rings of polystyrene and the existence of a partial clustering of the metal atoms /8/. The
present measurements on PSt/Ru \( n=2 \) confirm the previous results: the FT (Fig.1b) is characterized by a peak at \( \sim 1.4 \) Å, attributed to Ru-C coordination, and by a second peak at \( \sim 2.5 \) Å, assigned to Ru-Ru coordination.

From the comparison among the three FT in Fig.1 one can deduce that:

a) in all three compounds ruthenium is complexed to single phenyl rings (main peak at \( \sim 1.4 \) Å); 
b) there is no clear evidence of a Ru-Ru peak (at \( \sim 2.5 \) Å) for the compound PSt/Ru \( n=1 \); however, in view of the small signal to noise ratio of the experimental spectrum, a partial clustering of Ru cannot be excluded for this compound; 
c) the Ru-Ru peak for the sample PSt/Ru \( n=2 \) subjected to a catalytic run (Fig.1c) is higher than for the starting compound (Fig.1b), indicating that the hydrogenation process favors the clustering of ruthenium.

To study the life of the PSt/Ru \( n=2 \) catalyst we have recovered the sample from a catalytic hydrogenation run of benzene to cyclohexane /6/ and reused it in a second analogous catalytic run. Fig.2a shows the EXAFS spectrum after the first hydrogenation reaction. The Ru-C and Ru-Ru coordinations have been quantitatively analyzed by backtransforming the real space spectra in the range 1.2–3 Å; the single contributions of the two shells cannot be completely separated owing to the interference of the Ru side lobe with the C peak.

The results given in Table I have been obtained by a standard two-shell fitting procedure; the theoretical phaseshifts and amplitudes from Teo and Lee have been utilized for the Ru-C bond, the experimental ones (extracted from the EXAFS of polycrystalline Ru) for the Ru-Ru bond.

\[ \begin{align*}
\text{Table I} & \\
\text{Ru-C bond:} & \\
\text{Experimental} & \\
\text{Theoretical} & \\
\end{align*} \]

\[ \begin{align*}
\text{Ru-Ru bond:} & \\
\text{Experimental} & \\
\text{Theoretical} & \\
\end{align*} \]
The best fit has been obtained in the range $k=6-12$ Å$^{-1}$ (Fig.2b). The agreement factor resulted less than 3% for the two samples. For $k$ lower than 6 Å$^{-1}$ the quality of the fit was worse: this can be due to the inadequacy of the theoretical phaseshift and amplitude of carbon and/or the utilization of the same free parameter $E_0$ for both shells (C and Ru).

From the data of Table I one can deduce that the mean diameter of the ruthenium clusters does not exceed about 10 Å and that the local coordination of the Ru atoms does not change, within the experimental uncertainty, at least in the first catalytic cycles, pointing out the good stability of these catalysts.

As a consequence of the results here reported, further EXAFS data will be collected to study how the catalytic properties of these polymer/metal systems depend on the Ru content and to know the structure of the catalyst both in the first steps of the hydrogenation reaction and after many catalytic runs.

### TABLE I

EXAFS results for the PSt/Ru compound n=2 subjected to 1 and 2 catalytic runs. The distances are in Å.

<table>
<thead>
<tr>
<th></th>
<th>Ru-C</th>
<th></th>
<th>Ru-Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r$ N $\sigma^2$</td>
<td></td>
<td>$r$ N $\Delta\sigma^2$</td>
</tr>
<tr>
<td>1 run</td>
<td>2.01±0.02 4.5±1 0.0065</td>
<td></td>
<td>2.67±0.02 5.0±1 0.043</td>
</tr>
<tr>
<td>2 runs</td>
<td>2.01±0.02 4.4±1 0.0076</td>
<td></td>
<td>2.67±0.02 5.9±1 0.054</td>
</tr>
</tbody>
</table>

**REFERENCES**

/1/ Y.Chauvin, D.Commereuc and F.Dawans, Progr. Polym. Sci. 5 (1977) 95


