AXAFS studies on ruthenium(II) complexes used in interphase catalysis

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Interphases are systems in which a stationary phase (comprising of active centers, polymer and spacer) and a mobile component (gas, liquid or dissolved reactants) penetrate each other on a molecular scale without forming a homogeneous phase. When such interphases are provided with a swellable polymer, they will be able to imitate homogeneous conditions as the active centers become highly mobile simulating the properties of a solution. In such systems, the catalysts are easily separable from the reaction products and can be used for several cycles [1]. A vital aspect in the interphase systems is the study of electronic properties of the active metal center, which is influenced by the coordinating ligands. Atomic X-ray absorption fine structure (AXAFS) spectroscopy is a sensitive tool to study the charge densities that are responsible for bonding and to determine the electronic structure of the metal center. AXAFS arises from scattering within the absorbing atom due to the backscattering of the photoelectron at charge densities around the absorbing atom. The intensity and position of the AXAFS features is a function of the bonding of the absorbing atom with its environment [2].

The transmission mode X-ray absorption fine structure (XAFS) measurements of the samples were performed at the Ru K-edge at 22117 eV at the beamline X1.1. The samples were measured with Si(311) double crystal monochromator at ambient conditions and ion chambers filled with argon was used to measure the incident and transmitted intensities. AXAFS features arise from the difference between the free atom potential and the absorbing atom potential. The objective is to remove the contributions due to unbound absorbing atom and consider only those from the absorbing atom bound to its neighbours. The AXAFS contributions may overlap with the multiple electron excitations (MEE) and Ramsauer-Townsend resonances (RTR) at the low r-ranges, and with EXAFS oscillations at the high r-ranges. Hence, both these features need to be separated from the AXAFS signals. For this purpose, the criteria used for the background removal, outlined in literature [3] was employed. The program AUTOBK was used for the AXAFS background removal. Calculations were performed with different sets of r_{bkg} (refers to the upper limit of the low r-region over which the background is to be fit) values on a specific sample, namely, diphenyl (ether-phosphine) ruthenium(II) complex and the best r_{bkg} value was selected. The chosen value was used in the isolation of the AXAFS signal from the background for all the other samples. It is always possible that the choice of the r_{bkg} value does not lead to an optimal separation between MEE, AXAFS and EXAFS. However, it should be noted that even without an optimal background subtraction, identical trends in the final AXAFS data could still be found as long as the background subtraction is performed consistently [3]. The final trend in the AXAFS areas will be same even though the absolute areas may be different. The data analysis in k space was performed using curved wave formalism of EXCURV98 with XALPHA phase and amplitude functions and the resulting $\chi(k)$ function was weighed with k^1.

AXAFS represents the scattering from the potential of the electron cloud of the absorber atom itself. The potential is dependent on the chemical and electronic environment of the absorbing atom and can be influenced by the different ligands. As the catalytic activity was observed to be different for the complexes with different ligands [4,5], AXAFS investigations were performed on three selected complexes, which have the same coordination environment around the ruthenium nucleus but with different ligands, as shown in Figure 1. The investigations are aimed at studying the influence of the different ligands on the electronic structure of the ruthenium(II) complexes. The AXAFS signal was isolated from total XAFS, by subtracting the fitted EXAFS contribution from the experimental spectrum using the procedure mentioned in literature [3]. The experimentally determined Fourier transforms (FT) illustrating the AXAFS features are shown in Figure 1. Since the polarisation of the absorbing atom can be correlated with electronegativity (EN) of the neighbouring atoms, the AXAFS determined parameters are compared with the sum of the electronegativity values of the neighbouring atoms (N refers to the coordination number of the neighbouring atom) in Table 1.

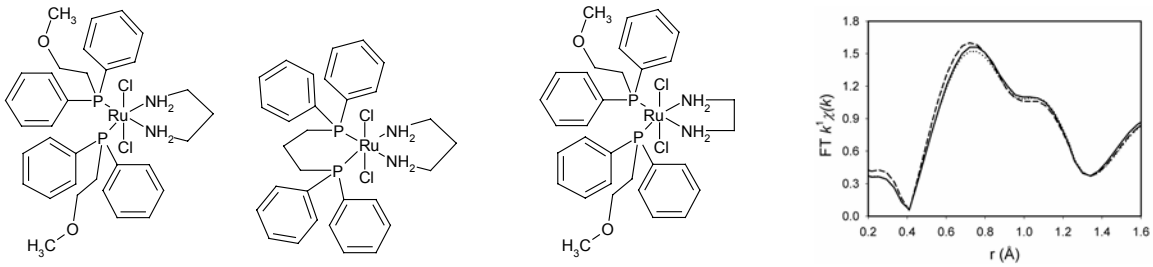

Figure 1. Structure of ruthenium(II) complexes **1**, **2** and **3** (with different ligands). Experimentally determined Fourier transforms of the AXAFS spectra of complexes **1** (solid line), **2** (dotted line) and **3** (dashed line), measured at Ru K-edge.

Table 1. AXAFS determined parameters compared with the electronegativity values

Complex	r-range [Å]	Position [Å]	Intensity	Area [Å^2]	Neighbours	EN	N	Overall EN	Sum EN
1	0.41 - 1.34	0.74 1.07	1.57 1.09	0.9434	N P Cl	3.0 2.1 3.0	2 2 2	6.0 4.2 6.0	16.2
2	0.41 - 1.34	0.74 1.07	1.52 1.09	0.9313	N P Cl	3.0 2.1 3.0	2 2 2	6.0 4.2 6.0	16.2
3	0.41 - 1.34	0.72 1.07	1.61 1.06	0.9541	N P Cl	3.0 2.1 3.0	2 2 2	6.0 4.2 6.0	16.2

In the AXAFS spectra, even though no remarkable changes could be observed in the peak shapes and positions (emphasising that the local structure around the ruthenium nucleus is the same in all the three cases), changes could be observed in the AXAFS intensity (quantified by FT area) between the complexes with different ligands, which could be attributed to the changes in the electron density around the ruthenium atom. The complexes **1** and **2** have nearly the same structure; the only difference is that the complex **1** has ether-phosphine ligand, whereas the complex **2** has diphosphine ligand. As a result, these two complexes have different electronic structure around the central ruthenium atom, as revealed by AXAFS. The observed differences in the electronic properties can be correlated with the catalytic activity of these two complexes (**1** and **2**). In the selective hydrogenation of *trans*-4-phenyl-3-butene-2-one, complex **1** yields 80% of *trans*-4-phenyl-3-butene-2-ol and 20% of 4-phenyl-2-butanol, whereas complex **2** yields 100% of *trans*-4-phenyl-3-butene-2-ol [4,5]. The AXAFS studies indicate that the polarisation of the absorbing atom by the neighbours (including far atoms) is due to space field effects, where the transmission of charge takes place through space due to the intramolecular columbic interaction between the active metal center and a remote unipole or dipole.

References

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