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Energy Dispersive EXAFS Performance Studies on Triphodalphosphine Rhodium Biphasic Catalyst for Hydrogenation and Hydroformylation of Olefins

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Energy dispersive EXAFS (EDE) data have been analyzed for the hydrogenation of styrene by the rhodium zwitterionic Rh(I) complexes, Rh(sulphos)(cod) and hydroformylation of 1-hexene by the Rh(sulphos)$(CO)_2$ using curved wave theory with *ab initio* phase-shifts. The derived parameters for metal compounds were in good agreement within experimental error of 0.02–0.05 Å for the bond distances. The bond lengths in the rhodium complexes were refined at average distances of Rh-C 1.90 Å, Rh-P 2.31 Å and Rh-O 2.90 Å consistently. This is a good start for the quantitative analysis of the dispersive EXAFS techniques at variable temperatures and high pressures.

Key Words: Energy dispersive EXAFS, Triphodalphosphine rhodium biphasic catalyst, Hydrogenation, Hydroformylation, Olefins.

INTRODUCTION

Transition metal complexes of the tripodal polyphosphine $CH_3C(CH_2PPh_2)_3$ have been studied for their chemistry[1] and potential as catalysts in several homogeneous reactions, including hydrogenation of alkynes, alkenes[2] and organic nitriles[3] and hydroformylation and isomerization of alkenes[4,5]. Recently, modification of the widely used triphos **1** gave a tridentate ligand **2**, sulphos, $Na\text{-}(p\text{-}SO_3(C_6H_4)CH_2C(CH_2PPh_2)_3)$, which has very low miscibility in hydrocarbons but is soluble in light alcohols. The hydrophilic sulphonated tail other than making the complex soluble in polar solvents, offers the possibility of grafting the metal complex onto an inorganic support for gas-solid and liquid-solid catalysts.

The zwitterionic Rh complex, Rh(sulphos)(cod) **3** has been prepared[6] and successfully characterized by FT-IR and solid state NMR. Preliminary NMR investigations have been carried out by Bianchini[6] and co-workers using Rh(sulphos)(cod) in the hydrogenation of styrene and in the hydroformylation of hexene, giving remarkably high conversion rates. Energy dispersive EXAFS was

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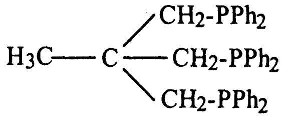
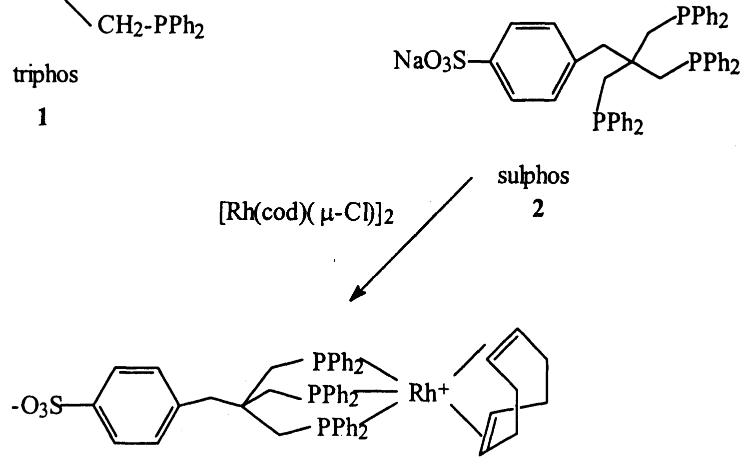
employed in order to investigate the intermediates, which may occur throughout the reactions and the species present in the homogeneous liquid phase.



triphos
1



Rh(sulphos)(cod)
3

EXPERIMENTAL

Experiments were conducted at ID24, ESRF. Scans were collected for Rh K-edge (23.2 keV) using a Si(III) Laue monochromator and employing an 1142 × 1252 pixels, cooled CCD camera (220 ms deadtime). The camera is operated in a streak mode, shifting the illuminated lines (1 to 64 lines) under a mask directly attached to the CCD[7]. The read-out time (3–9 s) limited the repetition of the time resolution (100 μs) for each spectrum[8]. Furthermore, the potential use of EDE in the future has been shown using variable pressure and temperature methods using a modified cell used in previous EXAFS studies of carbonylation catalysis[9, 10]

EDE analysis of the hydrogenation of styrene

Solid Rh(sulphos)(cod) (0.235 g, 0.25 mmol) was added to a solvent mixture of methanol : heptane of ratio 1 : 1 (10 mL) under flowing argon. The yellow solution contained two phases: the rhodium complex dissolved in methanol (bottom layer) and heptane (top layer). Styrene (0.57 mL, 5 mmol) was syringed into the solvent mixture to give a catalyst to substrate ratio of 1 : 20 in solution. Air was evacuated from a stainless steel EXAFS cell (see Appendix III.3) several times before leaving it under a flow of argon for 5 min. The catalyst and substrate solution (2 mL) was injected into the cell (to fill 1/3 of the cell volume). H_2 was introduced slowly up to 5 bar and the stirrer was switched on. In order to study EDE *in situ*, the stirrer was switched off and the cell was heated to the desired temperature of 65°C prior to EDE measurements. Data were acquired at 50 accumulations, 2.0 ms integration time and using acetone in the I_0 cell. PET (2 mm thickness) was used for the cell windows. The reaction was cooled down to room temperature after the measurement.

EDE analysis for the hydroformylation of 1-hexene

The procedure was analogous to that described for hydrogenation of styrene but using 1-hexene (0.62 mL, 5 mmol). The hydroformylation of 1-hexene is catalyzed by Rh(sulphos)(cod) in methanol-isooctane. After the injection of the catalytic solution into the cell, the addition of 5 bar of H_2 and 3 bar of CO, respectively into the cell. The stirrer was switched on and switched off prior to EDE measurement. The heater was set up at 70°C for first EDE measurement and set up at 85°C for another 100 EDE continuous run. Boron nitride windows (2 mm thickness) were used for higher pressure experiments in both sample and I_0 cells. The reactions were monitored using water in the I_0 cell at 50 accumulations with 15.0 ms sample integration time and 23.0 ms I_0 integration time. The reaction was cooled down to room temperature after 2 h.

RESULTS AND DISCUSSION

EDE analysis of the hydrogenation of styrene

The Rh(sulphos)(cod) complex **3** dissolves in methanol but not in heptane giving a well separated phase at room temperature in the mixed solution of methanol : heptane (1 : 1). Using clear PET windows, we could see the different phases but it is difficult to acquire the data for the rhodium complex in methanol in the bottom layer. Preliminary NMR studies[6] showed that in the presence of Rh(sulphos)(cod), styrene is hydrogenated to ethylbenzene at 65°C, after 3 h under 30 bar of H_2. To monitor this reaction using EDE, a reduction to 5 bar of H_2 was used in the modified high pressure EXAFS cell (20 mm path-length). Initially, a first test for the hydrogenation reaction, carried out in the absence of styrene, was acquired within 50 accumulations, 19.0 ms sample (I_t) integration time and 13.0 ms I_0 integration time. The 100 spectra took approximately 1 h with approximately 36 s for each spectrum.

When the temperature was increased to 65°C, the solution appeared as a yellow homogeneous liquid phase. The methanol : heptane mixture does not form a homogeneous phase at 65°C without Rh(sulphos)(cod). Analysis of the Rh K-edge EXAFS at this temperature, and its Fourier transform, after 6 min is shown in Fig. 1. The main peak in the Fourier transform is best fitted to donor atoms of the sulphos ligand which consists of 3.1 (3) phosphorus atoms at 2.330 (7) Å. The Rh-P distance is comparable with EXAFS analysis of complex **3** in the solid state (Rh-P, 2.3 Å)[11]. Attempts to fit the second shell with four carbon atoms from the cod ligand failed, leading to an unrealistic coordination number and high Debye-Waller factors. Based on **Scheme-1** for homogeneous hydrogenation[12], the analysis of EDE is consistent with the species **4**, on addition of H_2. The cod ligand appears to have disappeared and been replaced by hydride species. Analysis of the EDE spectrum after 1 h is consistent with species **4** being in the homogeneous phase as the 3.0 (4) phosphorus atoms remained at 2.310 (8) Å. The analyzed Rh

K-edge EXAFS and its Fourier transform is displayed in Fig. 2. (Table-2 shows the parameters derived from the fit.)

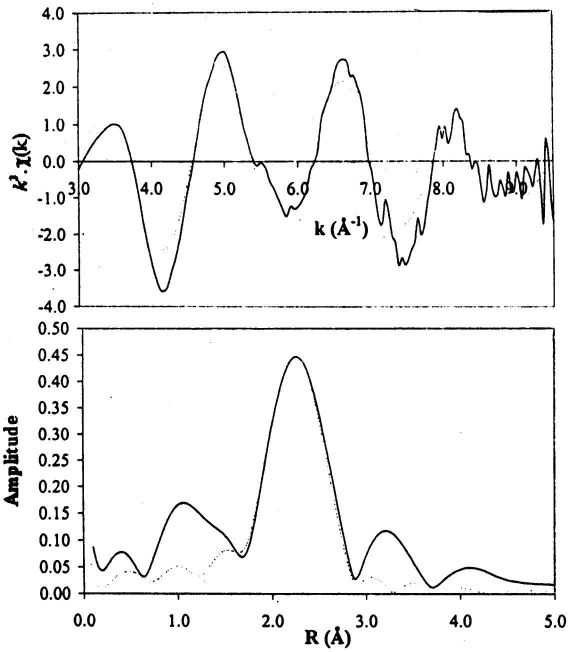
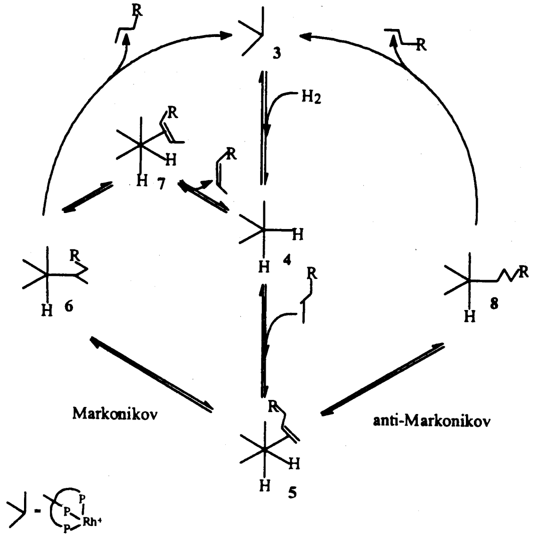


Fig. 1. The 10th EDE spectrum analyzed for the RhK-edge background subtracted k^3-weighted EXAFS spectrum and Fourier transform of the reaction of Rh(sulphos)(cod) with H_2 at 65°C after 6 min. The spectra were recorded at 50 accumulations with 19.0 7 ms (each spectrum took approximately 36 s).



Scheme 1. Mechanism proposed for the hydrogenation of styrene

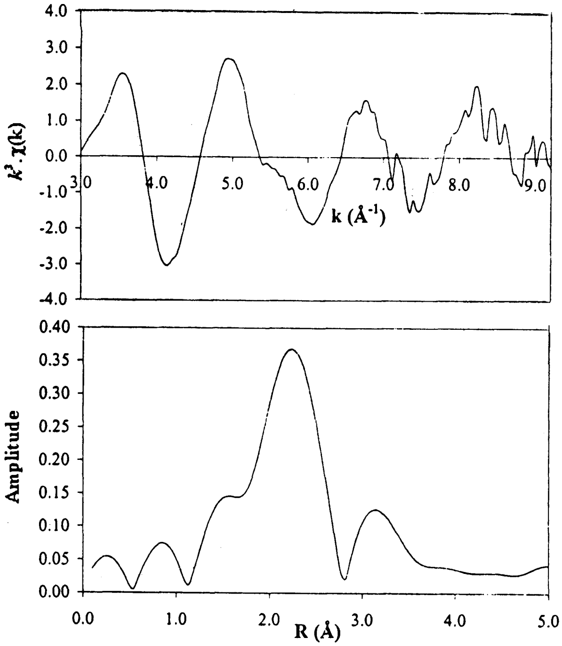


Fig. 2. The EDE Rh K-edge background subtracted k^3-weighted EXAFS spectrum and Fourier transform of the Rh(sulphos)(cod) with H_2 at 65°C after 60 min. The spectrum is taken from the final spectrum (100th EDE spectrum) with acquisition time of 50 accumulations, 19.0 ms (each spectrum took approximately 36 s),

TABLE-1

EDE SPECTRUM DERIVED PARAMETERS OF THE Rh(sulphos)(cod) AT 65°C AFTER 6 min OF REACTION WITH H_2 RECORDED AT 50 ACCUMULATIONS WITH 19.0 ms

EF = 0.006 eV, R = 49.41%, FI = 0.00278

Shell	CN	R_{EDE} (Å)	a($2\sigma^2$/Å^2)
P	3.1 (3)	2.330 (7)	0.023 (3)

Statistical errors are given in parentheses.

TABLE-2

EDE SPECTRUM DERIVED PARAMETERS OF THE REACTION OF Rh(sulphos)(cod) WITH H_2 FOR THE 100th EDE SPECTRUM AT 65°C AFTER 1 h (ACQUISITION TIME, 50 ACCUMULATIONS × 19.0 ms)

EF = 2.00 eV, R = 46.07 %, FI = 0.00248

Shell	CN	R_{EDE} (Å)	a($2\sigma^2$/Å^2)
P	3.0 (4)	2.310 (8)	0.028 (1)

Statistical errors are given in parentheses.

TABLE-3

EDE SPECTRUM DERIVED PARAMETERS OF THE 10th EDE SPECTRUM OF THE HYDROGENATION OF STYRENE BY Rh(sulphos)(cod) AT 65°C AFTER 5.5 min

The spectra were acquired at 50 accumulations with 14.0 ms.

EF = 4.35 eV, R = 32.63%, FI = 0.00102

Shell	CN	R_{EDE} (Å)	a($2\sigma^2$/Å^2)
C	2.3 (2)	1.989 (27)	0.008 (2)
P	2.9 (3)	2.296 (34)	0.012 (4)

Statistical errors are given in parentheses.

Following the hydrogenation of styrene, a first EDE attempt was made at a higher concentration of rhodium solution, [Rh] (25 mM), but the lower pressure of 5 bar of H_2 (actual NMR experiments, [Rh] (5 mM), 30 bar of H_2). After increasing the temperature up to 65°C, the 10th spectrum of 100 consecutive spectra (after 5.5 min) taken at 14.0 ms sample integration time, 14.0 ms I_0 integration time and 50 accumulations was analyzed. In the Fourier transform (Fig. 3), the main peak comprises two coordination shells of 2.3 (2) carbon atoms fitted at 1.989 (27) Å and 2.9 (3) phosphorus atoms at 2.296 (34) Å from the sulphos ligand. The appearance of the 2.3 carbons determined from the alkene group even under milder conditions using EDE is characterized for the η^2-olefin

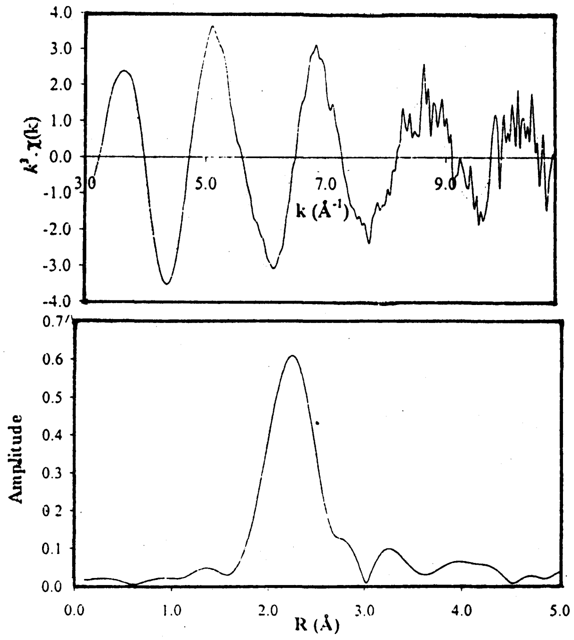


Fig. 3. The EDE Rh K-edge background subtracted k^3-weighted EXAFS spectrum and its Fourier transform phase-shift corrected for phosphorus of the hydrogenation of styrene by Rh(sulphos)(cod) at 65°C after 5.5 min. The spectra were acquired at 50 accumulations with 14.0 ms (each spectrum took 33 s).

intermediate **5**. This result is similar to the hydrogenation of ethene over a crystalline organometallic catalyst under mild conditions of 1 bar of H_2 at 60°C[13].

From the spectrum analyzed in Fig. 4, it was found that the Markownikoff addition of hydride to a coordinated alkene, **6**, which is responsible for the double bond isomerization[14–16] and the anti-Markownikoff addition of hydride to a coordinated alkene, **8**, are difficult to distinguish in this reaction due to the free motion of the coordinated alkene groups. The thermal motion of the group increases the Debye-Waller factors. Fig. 4 shows the Rh K-edge EXAFS and its Fourier transform acquired from the 100th spectrum (within 1 h) is best fitted to the values summarized in Table-4. Two coordination shells were fitted to the main peak (Fourier transform windows from 1.1 to 3.7). The main peak consists of 1.2 (4) carbon atoms fitted at 2.038 (17) Å in the first coordination shell and 3.0 (3) phosphorus atoms could be fitted at 2.324 (16) Å in the second coordination shell. The appearance of the EXAFS data (after being treated with styrene and 5 bar of H_2 at 65°C) in Fig. 4 is different at the zero crossing compared to the spectrum of intermediates **4** (without styrene, at 5 bar of H_2 and 65°C) in Fig. 2. The zero crossing is different at 4.0, 4.7, 5.7 and 6.5 kÅ^{-1} compared to 3.7, 4.5, 5.4 and 6.2 kÅ^{-1} for the reaction without styrene.

Cooling the reaction to room temperature gave a separation of the phases with Rh complexes in the form of a soluble species, not yet identified, in the bottom layer and ethyl benzene products in heptane on the top layer. This liquid biphasic catalyst

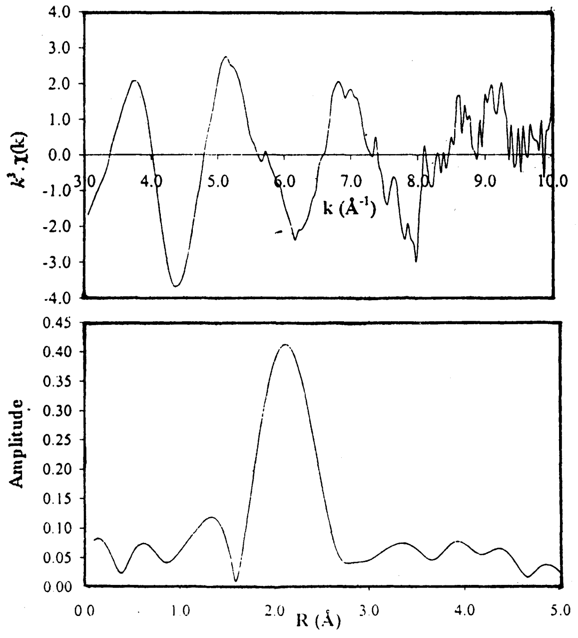


Fig. 4. The EDE Rh K-edge background subtracted k^3-weighted EXAFS spectrum and its Fourier transform phase-shift corrected for phosphorus of the hydrogenation of styrene by Rh(sulphos)(cod) at 65°C after 55 minutes. The spectra were acquired at 50 accumulations with 14.0 ms (each spectrum took 36 s).

system for hydrogenation of styrene showed that stepwise alkylation could be successfully monitored *in situ* using EDE at variable pressure and temperature and provides reliable structural information about the rhodium coordination sphere. In heterogeneous studies using EXAFS of the complex attached to the silica surfaces, the Rh(I) sites (after removal of the cod ligand) were found to be highly active for hydrogenation. Following the hydrogenation reaction, the cod ligand in the catalyst precursor was quantitatively converted to cyclooctene[6].

TABLE-4
EDE SPECTRUM DERIVED PARAMETERS OF THE 100th EDE SPECTRUM OF THE HYDROGENATION OF STYRENE BY Rh(sulphos)(cod) AT 65°C AFTER 55 min

The spectra were acquired at 50 accumulations with 14.0 ms.

EF = 4.01 eV, R = 52.72%, FI = 0.00322

Shell	CN	R_{EDE} (Å)	$a(2\sigma^2/Å^2)$
C	1.2 (4)	2.038 (17)	0.008 (1)
P	3.0 (3)	2.324 (16)	0.012 (1)

Statistical errors are given in parentheses.

TABLE -5
EDE DERIVED PARAMETERS OF THE REACTION OF Rh(sulphos)(cod) WITH H_2 (3 bar) + CO (5 bar) AT 70°C AFTER 5.5 min, ACCUMULATED AT 50 ACCUMULATIONS × 15 ms

EF = 2.03 eV, R = 78.47%, FI = 0.00746

Shell	CN	R_{EDE} (Å)	$a(2\sigma^2/Å^2)$
C	2.0	1.924 (26)	0.010
P	3.0	2.327 (54)	0.015
O	2.0	2.958 (48)	0.018

Statistical errors are given in parentheses.

TABLE-6
EDE DERIVED PARAMETERS OF THE HYDROFORMYLATION OF 1-HEXENE BY Rh(sulphos)(cod) with H_2 (3 bar) + CO (5 bar), AT 70°C AFTER 59 min

EF = 3.95 eV, R = 75.54%, FI = 0.00721

Shell	CN	R_{EDE} (Å)	$a(2\sigma^2/Å^2)$
C	2.0	1.925 (22)	0.010
P	3.0	2.329 (46)	0.015
O	2.0	2.934 (30)	0.018

Statistical errors are given in parentheses.

TABLE-7
EDE SPECTRUM DERIVED PARAMETERS OF THE 25th EDE SPECTRUM OF THE HYDROFORMYLATION OF 1-HEXENE BY Rh(sulphos)(cod) AT 85°C AFTER 20 min

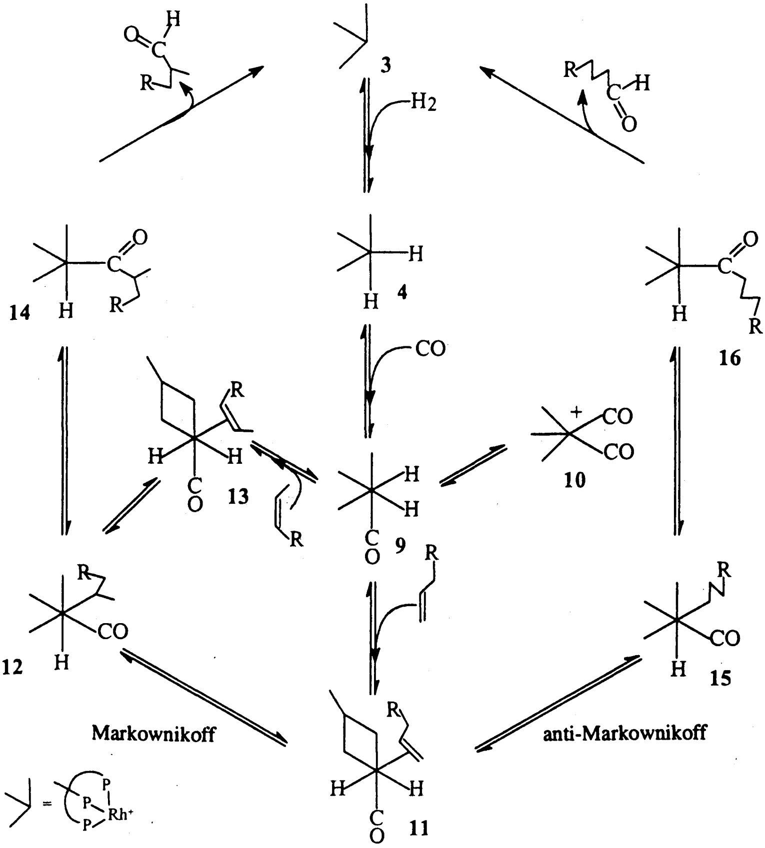
EF = 2.19 eV, R = 71.24%, FI = 0.00621

Shell	CN	R_{EDE} (Å)	$a(2\sigma^2/Å^2)$
C	1.0	1.884 (15)	0.010
P	3.0	2.311 (42)	0.015
O	1.0	2.912 (51)	0.018

Statistical errors are given in parentheses.

EDE analysis for the hydroformylation of 1-hexene

Two EDE measurements consisting of 100 EDE spectra each were acquired to determine the intermediates of the hydroformylation of 1-hexene. The NMR observation under these conditions detected only the inactive species of Rh(sulphos)$(CO)_2$ **10** as illustrated in **Scheme-2**. The actual NMR experiment used low



Scheme-2. Mechanism proposed for the hydroformylation of 1-hexene concentration of rhodium complex [5 mM] but the higher concentration used [25 mM] in EDE, required for transmission mode, gave poor solubility. In the first measurement, heating up to 70°C from room temperature gave better solubility of the homogeneous phase. Each spectrum was recorded approximately 34 s, for 100 EDE spectra. After approximately 5.5 min, investigation on the 10th spectrum gave best curve fitting for the species **10**. 2.0 carbon atoms from carbonyl groups are fitted to the first peak in the Fourier transform (Fig. 5) at 1.924 (26) Å. The second characteristic peak is dominated by 3.0 phosphorus atom at 2.327 (54) Å for the second shell.

Multiple scattering unit was employed to determine the CO groups, with a bond angle of 180° in the Rh—C—O. The third peak is assigned to the 2.0 oxygen atoms at 2.958 (48) Å from the carbonyl groups. The distances are comparable to the distances obtained on solid sample of Rh(sulphos)$(CO)_2$ (Rh—C 1.87 Å, Rh-P 2.31 Å and Rh-O 2.99 Å) using standard EXAFS[17].

To improve the quality of the spectrum, the last four spectra at the end of the reaction (47th, 48th, 49th and 50th) were averaged and background subtracted in PAXAS. The averaged spectrum gave a better quality of white line feature but still contained a high level of noise above 6 $kÅ^{-1}$. The Rh k^3-weighted EXAFS spectrum and Fourier transform shown in Fig. 6 were best fitted with three shells. The first shell is best fitted to 2.0 carbon atoms at 1.925 (22) Å. The second peak is determined as 3.0 phosphorus atoms at 2.329 (46) Å and the third shell is fitted

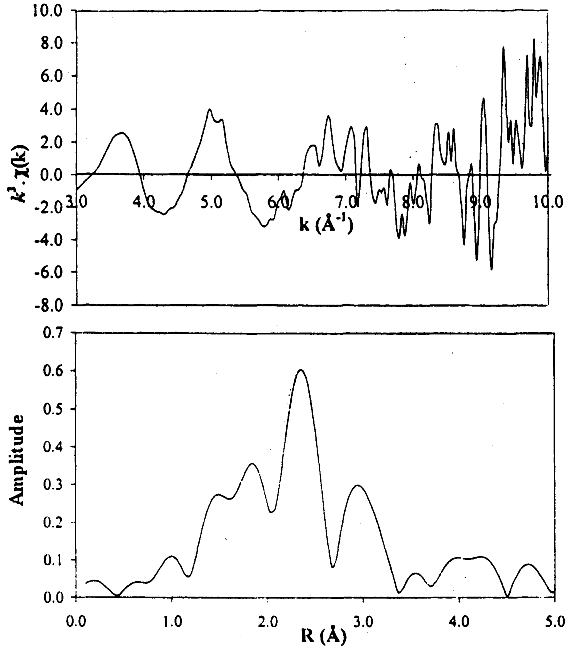


Fig. 5. The 10th EDE spectrum analyzed for the Rh K-edge k^3-weighted EXAFS spectrum and Fourier transform of the reaction of Rh(sulphos)(cod) with H_2 (5 bar) + CO (3bar) at 70°C after 5.5 min. The spectra were acquired at 50 accumulations with 15.0 ms (each spectrum took 34 s).

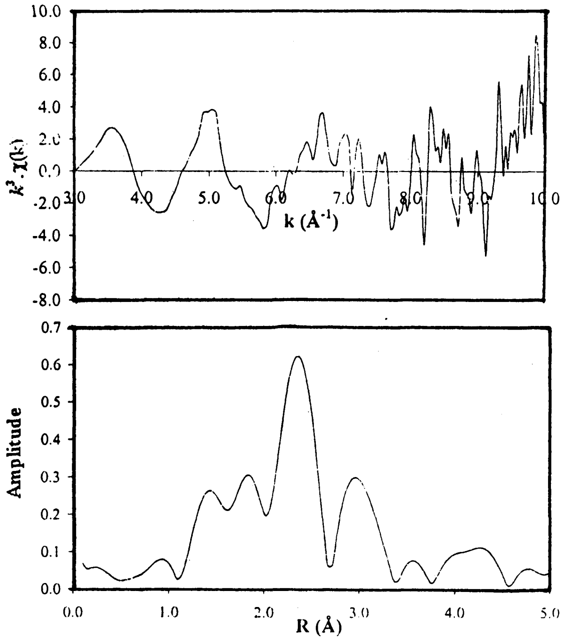


Fig. 6. EDE Rh K-edge k^3-weighted EXAFS spectrum and Fourier transform of the averaged spectrum of the hydroformylation of 1-hexene by Rh(sulphos)(cod) with H_2 (3 bar) + CO (5 bar), at 70°C after 59 min. The EDE spectra were acquired at 50 accumulations with 15.0 ms (each spectrum took 34 s).

by 2.0 oxygen atoms at 2.937 (30) Å suggesting that the appearance of 2 carbonyl groups and indicating species **10** dominates this reaction at 70°C, as observed in the previous spectrum.

After a reaction time of 1 h at 70°C, the second EDE measurement was set up at higher temperature at 85°C. Approximately after 20 min, assuming that the reaction is maintained at the desired 85°C, the 25th spectrum was best analyzed up to 10 K. The Fourier transform of the spectrum displayed 3 main features. One carbonyl group is represented by 1.0 carbon atoms at 1.884 (15) Å in the first shell and 1.0 oxygen atoms at 2.912 (51) Å in the third shell. The distance is 0.1 Å shorter than the one observed at 70°C. The second peak can be best fitted to 3.0 phosphorus atoms at 2.311 (42) Å, which represents the appearance of the sulphos ligand. Only intermediate **9** with one CO group could be determined from the analysis. The presence of any species with the coordinated alkene or alkyl group, *e.g.*, **11**, **12** or **14** are very difficult to model and differentiate in the multiple scattering analysis. The R-value achieved gave a good refinement at R = 68%. Further analysis of the spectrum after 2 h gave similar parameters derived for the spectrum after 20 min with the appearance of one carbonyl group and one sulphos ligand attached to the rhodium centre.

The solid-liquid hydroformylation of 1-hexene gave a conversion to aldehydes (heptanal, 2-methylhexanal and 2-ethylpentanal), but at longer times (5 h), only alcohol is produced[6].

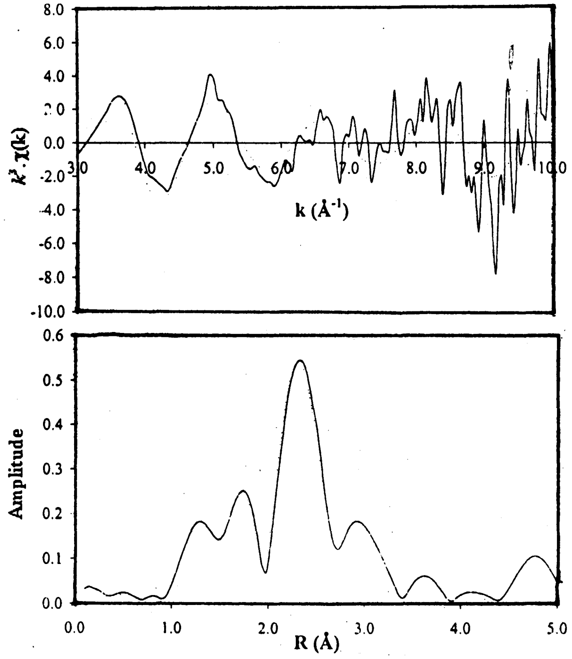


Fig. 7. EDE Rh K-edge k^3-weighted EXAFS spectrum phase-shift corrected for carbon and its Fourier transform of the 25th spectrum of the hydroformylation of 16 hexene by Rh(sulphos)(cod) with H_2 (3 bar) + CO (5 bar), at 85°C after 20 min. The EDE spectra were acquired at 50 accumulations with 15.0 ms (each spectrum took 34 s).

Conclusions

The solution cell equipped with PET or BN windows and liquid/gas inlet valves, working with variable temperature and pressure could be used in future for transmission EDE. The I_0 sample was changed to give a better absorption match for the EDE measurement. In the different catalytic runs using different solvents, acetone was found to give better results for the hydrogenation reaction, while water is better for the hydroformylation.

Following the hydrogenation of styrene by the zwitterionic Rh(I) complex, Rh(sulphos)(cod), in liquid biphasic system showed in **Scheme-1**, which were believed to be all the Rh species present. These catalytic runs were first attempts using energy dispersive EXAFS at varying concentration and pressure from established NMR studies revealed similar observation to the proposed mechanism. A perusal of the coordination around the active Rh centre gave bond distances of Rh—C 1.98 Å from the alkyl group and Rh—P 2.32 Å of the sulphos ligand. Investigation by NMR and EXAFS determined that after the removal of cod ligand, hydrogenation is highly active.

The hydroformylation of 1-hexene by the Rh complex giving the species Rh(sulphos)$(CO)_2$ with the derived distances of Rh—C 1.90 Å, Rh—P 2.31 Å and Rh—O 2.90 Å consistently. The EDE results showed that a variety of ligands are bonded to the rhodium centre but it is very difficult to distinguish the coordinated alkene. This is a good start for the quantitative analysis of the dispersive EXAFS techniques at variable temperatures and high pressures.

The multiple scattering unit is well defined with carbon and oxygen atoms (bond angles of 180°) from the carbonyl groups bonded to the rhodium atom. This enabled best modelling of the low k region, where the best signal to noise ratio is found. However, high noise levels after 6 $kÅ^{-1}$ limit the analysis and make it very difficult to investigate the surrounding atoms.

REFERENCES

1. C. Bianchini, P. Frediani, A. Meli, M. Peruzzini and P. Ramirez,. *Organometallics*, **9**, 226 (1990).
2. C. Bianchini, A. Meli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, **110**, 8725 (1988).
3. L.F. Rhodes and L.M. Venanzi, *Inorg. Chem.*, **26**, 2692 (1987).
4. C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, Y. Fujiwara, T. Jintoku and H. Taniguchi, *J. Chem. Soc. Chem. Commun.*, 210 (1988).
5. C. Bianchini, F. Laschi, A. Meli, M. Peruzzini, P. Zanello and P. Frediani, *Organometallics*, **7**, 2575 (1988).
6. C. Bianchini, P. Frediani and V. Sernau, *Organometallics*, **14**, 5458 (1995).
7. J. Borrel, M. Hagelstein, G. Marrot, M. Reneir and A. San-Miguel, *J. Synch. Rad.*, **5**, 1396 (1998).
8. C. Ferrero, M. Hagelstein, U. Hatje, W. Metz and T. Ressler, *J. Synchr. Rad.*, **2**, 174 (1995).
9. J. Evans, G. Jingxing, H. Leach and A.C. Street, *J. Organometal. Chem.*, **372**, 61 (1989).
10. N. Cruise, Ph.D Thesis, University of Southampton (1994).
11. G. Huttner, M. Fritz, V. Sernau, O. Walter and L. Zsolnai, *J. Organometal. Chem.*, **53**, 23 (1993).
12. B.R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).
13. ———, Homogeneous Hydrogenation, Wiley, New York (1973).
14. C. Bianchini, E. Farnetti, M. Graziani, K. Kasper and F. Vizza, *J. Am. Chem. Soc.*, **115**, 1753 (1993).
15. W.C. Bird, Transition Metal Intermediates in Organic Synthesis, Academic Press, New York (1968).
16. D. Evans, J.A. Osborn and G. Wilkinson, *J. Chem. Soc. (A)*, 3133 (1968).

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