



	Experiment title: XAS study of the preparation and activation of single-site active tungsten catalysts supported onto silica for selective olefin transformation	Experiment number: 01-01 995
Beamline: BM01B	Date of experiment: from: March 9 th 2013 to: March 10 th 2015	Date of report: Sept. 12 th 2015
Shifts: 1	Local contact(s): Ermann HEMERICH	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

LE ROUX Erwan*	University of Bergen, Department of Chemistry, Bergen, Norway
QUADRI Coralie*	University of Bergen, Department of Chemistry, Bergen, Norway
DE MALLMANN Aimery*	ESCPE-Lyon, C2P2 Lab., UMR5265 CNRS/UCBL, Villeurbanne, France
SZETO Kai Chung*	ESCPE-Lyon, C2P2 Lab., UMR5265 CNRS/UCBL, Villeurbanne, France
BOUHOUTE Yassine*	ESCPE-Lyon, C2P2 Lab., UMR5265 CNRS/UCBL, Villeurbanne, France
TAOUFIK Mostafa	ESCPE-Lyon, C2P2 Lab., UMR5265 CNRS/UCBL, Villeurbanne, France

Report:

This study was a one day continuation of project 01-01-905. The aim of this EXAFS study was to precise the structure of tungsten complexes supported onto silica, used as catalysts for olefin metathesis. The different steps of their elaboration had already been followed by chemical analyses and IR, Raman, solid-state NMR and EPR spectroscopies. A XAS study at the active W L_{III}-edge could help us to precise the evolution of the metal coordination sphere and consequently strengthened our knowledge about the activity-structure relationship of our systems.

This work led to a paper recently accepted at *ACS Catalysis*:

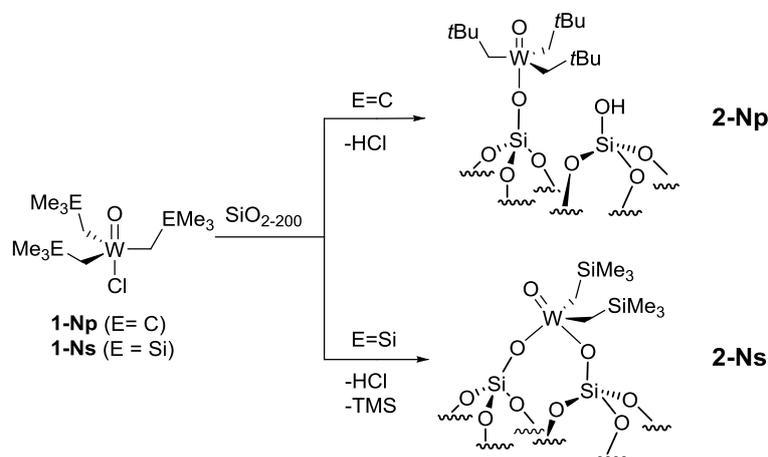
Accessing realistic models for the WO₃-SiO₂ industrial catalyst through the design of organometallic precursors.

Bouhoute, Y.; Grekov, D.; Szeto, K. C.; Merle, N.; De Mallmann, A.; Lefebvre, F.; Raffa, G.; Del Rosal, I.; Maron, L.; Gauvin, R.; Delevoye, L.; Taoufik, M. *ACS Catal.*, **2015**, *accepted*.

Abstract:

In order to access realistic models to the industrial olefin metathesis catalyst WO₃/SiO₂, that is a bigrafted tungsten oxo alkylidene species [(≡SiO)₂WO(=CHR)], we targeted the parent bis alkyl oxo derivative [(≡SiO)₂WOR₂] prone to carbene formation. Thus grafting of [WO(CH₂EMe₃)₃Cl] (E= C, **1-Np** and E= Si, **1-Ns**) onto silica dehydroxylated at 200 °C was performed. While **1-Np** affords monopodal

species $[(\equiv\text{SiO})\text{WO}(\text{CH}_2\text{CMe}_3)_3]$ **2-Np**, the neosilyl derivative **1-Ns** reacts to yield well-defined bipodal species $[(\equiv\text{SiO})\text{WO}(\text{CH}_2\text{SiMe}_3)_2]$ **2-Ns**, via consecutive HCl and SiMe₄ release. This was demonstrated by mass balance analysis, elemental analysis, IR, advanced solid-state NMR (1D and 2D ¹H, ¹³C, ²⁹Si and ¹⁷O) and EXAFS. Furthermore, DFT calculations allowed understanding and rationalizing the experimental results regarding grafting selectivity. Material **2-Ns** proved to be the most stable and efficient supported tungsten oxo catalyst for propene metathesis under dynamic conditions.



Scheme 1. Reaction of **1-Np** and **1-Ns** with SiO₂₋₂₀₀

EXAFS study:

The structural hypothesis for the grafted species **2-Ns** was further confirmed by a XAS study. This consisted in recording and analyzing the W L_{III}- EXAFS spectra of both the molecular complex **1-Ns** and the supported species resulting from its grafting onto SiO₂₋₂₀₀, in order to assess and compare the structures of the tungsten coordination sphere in both cases.

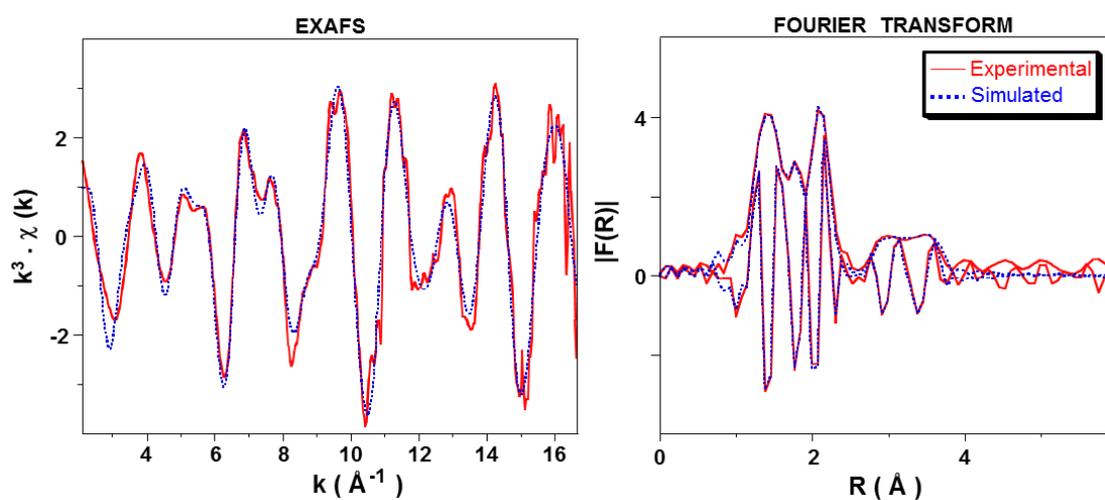


Figure 1. Tungsten L_{III}-edge k^3 -weighted EXAFS (left) and corresponding Fourier transform (right, modulus and imaginary part) with comparison to simulated curves for **1-Ns**. Solid lines: experimental; dashed lines: spherical wave theory.

For **1-Ns** (Figure 1 and Table 1), the results are consistent with the following coordination sphere around W: one oxygen atom at 1.694(8) Å, assigned to an oxo ligand, ca. three carbon at 2.10(1) Å, corresponding to σ -bonded carbon atoms of neosilyl ligands and one chloride at 2.41(1) Å. The W-C bond distance is in the same range as those found in the Me₃SiO-W(Ns)₃O moieties of the bimetallic complex [Me₃SiO-W(Ns)₃O-WNs₃(≡C-SiMe₃)] (2.084 to 2.106 Å for W-C),¹ while the W=O bond of these moieties (1.729-1.746 Å) being longer due to the bridging nature of the oxo ligand. The W=O bond distance in **1-Ns** is however typically in the range found for similar complexes, as for [O(WONp₃)₂],² with W=O in the range 1.676-1.736 Å (W-C: 2.113 to 2.150 Å) or for [OWCpNs₃],³ (1.664(8) Å for W=O, (W-C_{Ns}: 2.231 to 2.322 Å). Besides, similar W-Cl bond distances have been observed in [W^{VI}OCIX₃] type complexes: 2.397 and 2.427 Å for (μ^2 -oxo)-bis(benzoyltrifluoroacetato)-dichloro-oxo-tungsten(VI) (with a 1.696 Å W=O bond length),⁴ and 2.4212(2) Å for [WO(C₆H₁₂O₂)(C₆H₁₃O₂)Cl] (with a 1.716(3) Å W=O bond length).⁵ Similar parameters were obtained when fitting the k². χ (k) spectrum. Furthermore, the fit was improved when considering a further layer of three Si atoms back-scatterers at 3.43(3) Å, assigned to the Si of the neosilyl ligands. This corresponds to the distance found for the bi-metallic complex [Me₃SiO-W(Ns)₃O-W(Ns)₃(≡C-SiMe₃)] cited above: 3.423(6) to 3.442(6) Å,¹ where [W-C-Si] angles from 118.9(2)° to 119.1(3)° were found. The consideration of two multiple scattering O=W-Cl pathways also improved the fit, corresponding to a quasi linear arrangement of these three atoms in the complex (trans configuration), as proposed by Osborn et al. for [WO(Np)₃Cl].⁶ These experimental results are in excellent agreement with the DFT-calculated values.

Table 1. EXAFS parameters for complex **1-Ns** and DFT-calculated distances.^a

Type of neighbor	Number of neighbors	Distance (Å)	DFT-calculated distance (Å)	σ^2 (Å ²)
W=O	1.0(2)	1.694(8)	1.703	0.0015(5)
W-CH ₂ SiMe ₃	3.0(4)	2.10(1)	2.100 ^d	0.0030(9)
W-Cl	1.0(6) ^b	2.41(1)	2.456	0.0022(6)
W-CH ₂ SiMe ₃	3	3.43(3)	3.464 ^e	0.011(5)
MS ₃₁ O=W-Cl ^c	2	4.07(4)	-	0.003(3)
MS ₄₁ O=W-Cl ^c	2	4.07 ^b	-	0.003 ^b

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. ^a Δk : [2.2-16.6 Å⁻¹] - ΔR : [0.7-3.9 Å] ([0.7-2.5 Å], when considering only the first coordination sphere); $S_0^2 = 0.94$; $\Delta E_0 = 8.0 \pm 2.0$ eV (the same for all shells); Fit residue: $\rho = 6.4$ %; Quality factor: $(\Delta\chi)^2/\nu = 1.42$, with $\nu = 18 / 31$ ($[(\Delta\chi)^2/\nu]_1 = 2.93$ with $\nu = 9 / 18$, considering only the first coordination sphere: O, C and Cl). ^b Shell constrained to the parameters above. ^c These two multiple scattering pathways (three and four legs) have been considered in the fit, assuming a geometry close to linearity between these three atoms. ^d average value for 3 W-C distances. ^e average value for 3 W-Si distances

Figure 2 displays the W L_{III}- EXAFS spectrum of the species resulting from the grafting of **1**-Ns onto SiO₂₋₂₀₀, namely **2**-Ns. The nearly complete disappearance of the direct W-Cl and multiple (O=W-Cl) scattering pathways can be clearly observed from the comparison of the moduli of the Fourier transforms of both molecular and supported species (contribution of the Cl back-scatterer at ca. 2.1 Å and of the multiple scattering pathways at ca. 3.7 Å on the right part of Figure 2). The parameters extracted from the fit of the EXAFS spectrum (Table 2) agree with one oxo ligand at 1.693(6) Å, ca. two oxygen atoms at 1.86(1) Å and two carbon atoms at 2.11(1) Å and ca. 0.1 chlorine at 2.40(1) Å respectively assigned to ca. two siloxide, two neosilyl ligands and very few residual chlorine, consistently with W=O W-C and W-Cl bond distances found in tungsten oxo complexes (see above) and with the two O-W bond distances in the range of 1.852(2)-1.866(8) Å found in O=WNS₂(Me₄pyde) (pyde = 2,6-pyridinediethanolate; 1.708(8)-1.711(9) Å for W=O and 2.204(12)-2.236(15) Å for W-C). The shorter W-O distance found for these ≡SiO-W moieties compared to the one obtained for [≡SiO-WONp₃] (1.98(2) Å)⁷⁻⁹ may indicate that the oxo and a siloxy ligand are not fully *trans* to each other in this surface complex which may be slightly distorted compared to an ideal TBP geometry. Similar parameters were obtained when fitting the k²·χ(k) spectrum. The fit was also improved by adding two layers of silicon back-scatterers, both at 3.51(3) Å, one composed of ca. two silicon atoms, accounting for the quaternary silicons of the neosilyl ligands and another one with ca. two silicon atoms from to silicon atoms of surface siloxide ligands. These two layers were placed at the same distance from the W center in order to simplify the fit, and also because the resolution of the spectrum (ca. 0.09 Å) might be close to the difference between the distances of the two types of silicon from the tungsten center.

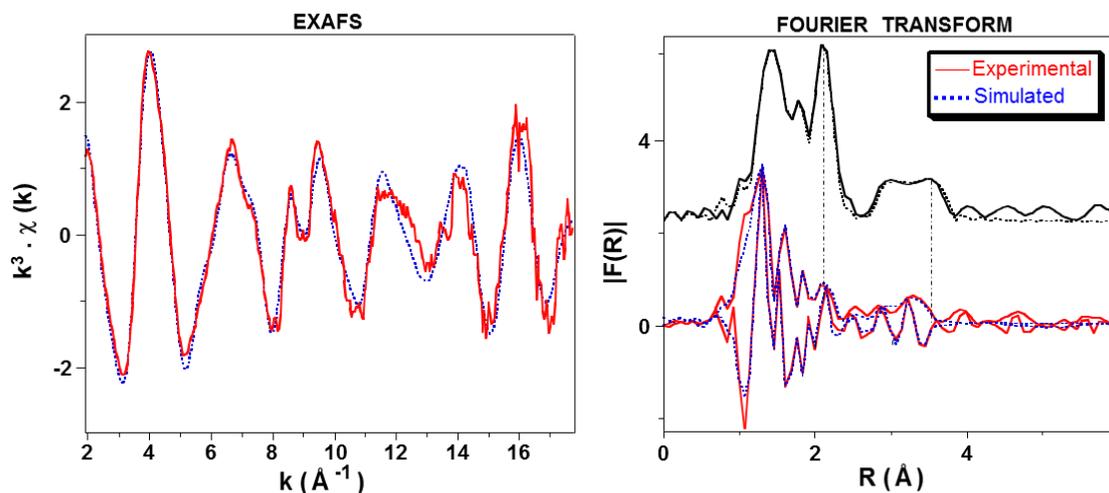


Figure 2. Tungsten L_{III}-edge k³-weighted EXAFS (left), of **2**-Ns and corresponding Fourier transform (right; modulus and imaginary part; in black: Fourier transform corresponding to complex **1**-Ns for comparison), superimposed with simulated curves. Solid lines: experimental; dashed lines: spherical wave theory.

Table 3. EXAFS parameters for the supported complex **2-Ns** and DFT-calculated values.^a

Type of neighbor	Number of neighbors	Distance (Å)	DFT-calculated distances (Å)		σ^2 (Å ²)
			TBP geometry ^d	SP geometry ^e	
W=O	1.0(1)	1.693(7)	1.712	1.692	0.0017(5)
W-QSi≡	2.1(2)	1.86(1)	1.939 ^f	1.928	0.0068(9)
W-CH ₂ SiMe ₃	1.8(2)	2.11(1)	2.098	2.140	0.0075(25)
W-Cl	0.1(5) ^b	2.40(1)	-	-	0.0025(9)
WCH ₂ SiMe ₃	1.8 ^b	3.51(3)	3.445	3.489	0.018(12)
W-OSi≡ ^c	2.1 ^b	3.51 ^b	3.515 ^f	3.407	0.0094(30)

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. ^a Δk : [1.9-17.7 Å⁻¹] - ΔR : [0.6-3.9 Å] ([0.6-2.4 Å], when considering only the first coordination sphere); $S_0^2 = 0.94$; $\Delta E_0 = 6.9 \pm 1.0$ eV (the same for all shells); Fit residue: $\rho = 6.3$ %; Quality factor: $(\Delta\chi)^2/\nu = 2.07$, with $\nu = 18 / 35$ ($[(\Delta\chi)^2/\nu]_1 = 4.15$ with $\nu = 8 / 20$, considering only the first coordination sphere: O, C and Cl). ^b Shell constrained to the parameters above. ^c Two (W-O-Si) types multiple scattering pathways (3 and 4 legs) have also been considered in the fit but not mentioned in this table. ^d Trigonal bipyramidal geometry, average values for both the **ac** and **b** models-derived species **2^b-Ns_{bi}** and **2^{ac}-Ns_{bi}**, Table S1. ^e Square pyramidal geometry, average values for both the **ac** and **b** models-derived species **2^b-Ns_{bi}** and **2^{ac}-Ns_{bi}**, Table S1. ^f average value for the chemically distinct siloxyde moieties, namely in *cis* and *trans* position to the apical oxo ligand (see Table S1 for the individual distances).

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