



	Experiment title: XAS study of the preparation and activation of single-site active catalysts supported on periodic mesoporous silica for selective olefin	Experiment number: 01-01 905
Beamline: BM01B	Date of experiment: from: July 15 th 2013 to: July 19 th 2013 (no beam on 16-17 th)	Date of report: Sept. 12th 2015
Shifts: 9	Local contact(s): Ermann HEMERICH	<i>Received at ESRF:</i>

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Report:

The aim of this study was to precise the structure of transition metal complexes supported on hybrid material, used as catalysts for different reactions involving olefin valorization as olefin oligomerization and metathesis. The different steps of their elaboration had already been followed by chemical analyses and IR, Raman and solid-state NMR or EPR spectroscopies. A XAS study at the active metal K (Zn, Nb) or LIII (Ta, W) edges will help us to precise the evolution of its oxidation state and coordination sphere and consequently strength our knowledge about activity-structure relationship of our systems, for a future rational development of novel tailor-made hybrid material catalysts.

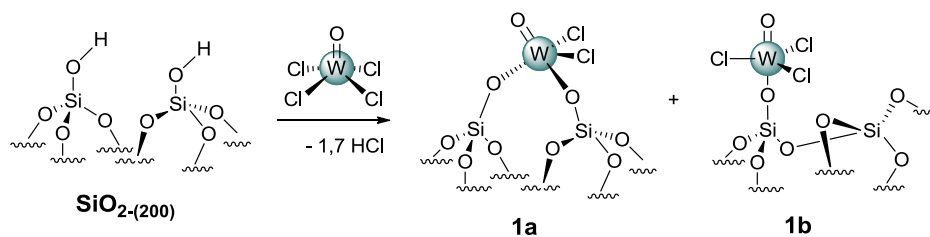
Up to now three papers have been written, two on the preparation, characterization and use of silica supported tungsten catalysts (*ACS Catalysis*: one published in 2014 and one accepted) and one on the preparation and characterization of zinc catalysts supported on mesoporous silica (submitted to *Organometallics*).

First paper: Well-defined supported mononuclear tungsten oxo species as olefin metathesis pre-catalysts.

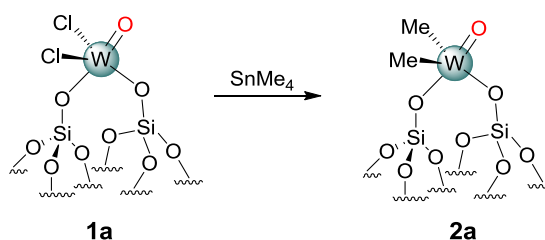
Bouhoute, Y.; Garron, A.; Grekov, D.; Merle, N.; Szeto, K. C.; De Mallmann, A.; Del Rosal, I.; Maron, L.; Girard, G.; Gauvin, R. M.; Delevoye, L.; Taoufik, M. *ACS Catal.*, **2014**, *4*, 4232-4241.

Extended abstract: The grafting of [WOCl₄] on SiO₂₋₂₀₀ under controlled conditions, leading to sample **1₂₀₀**, was studied using experimental and theoretical approach. Combination of spectroscopic evidence backed up by DFT calculations demonstrated that the grafting results in bipodal tungsten oxo bischloride surface species

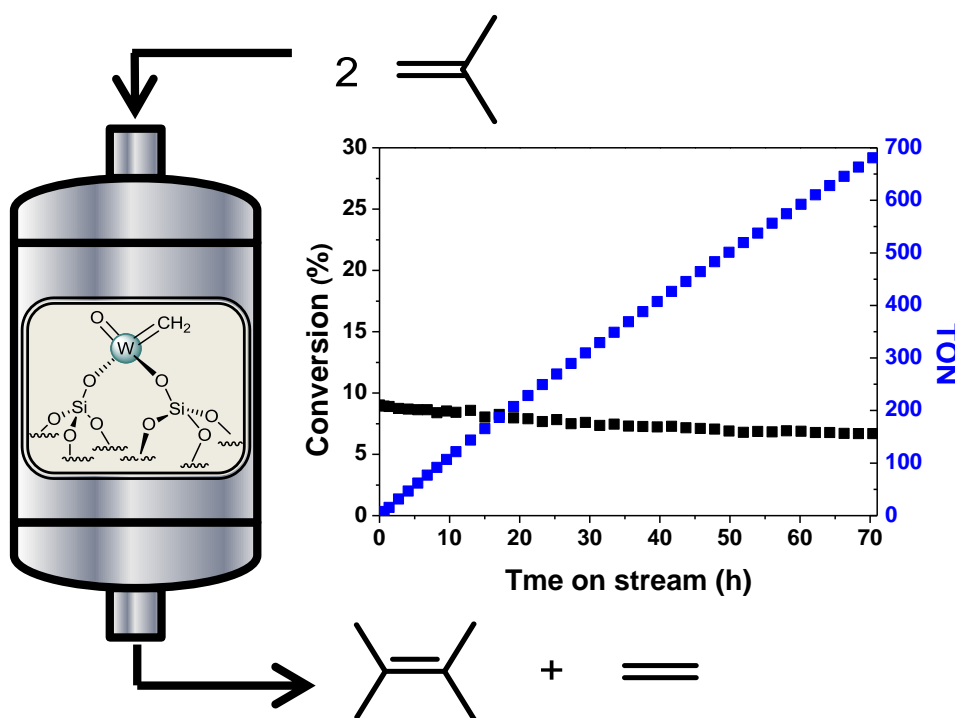
$[(\equiv\text{SiO})_2\text{WOCl}_2]$ (**1a**) as the major component, along with minor monopodal tungsten oxo trichloride centers $[(\equiv\text{SiO})\text{WOCl}_3]$ (**1b**). ^{17}O NMR demonstrated that both these centers adopt a square pyramidal configuration, with the oxo ligand in apical position.



Further treatment with SnMe_4 , leading to sample **2₂₀₀**, results in Cl/Me exchange within the surface species, as shown mainly by EXAFS and ^1H and ^{13}C MAS NMR.



This material is active in alkene metathesis, achieving efficient conversion of the challenging isobutene substrate. Importantly, this catalyst shows high stability and selectivity towards ethylene and 2,3-dimethyl-2-butene.



The reaction proceeds most probably by generation of bipodal tungsten oxo carbene species that resembles the proposed model for the industrial metathesis catalyst WO_3/SiO_2 : Further studies will be devoted to the selective preparation and the characterization of such species, and to the assessment of its catalytic performances.

EXAFS characterization of sample **1₂₀₀**: The characterization of Sample **1₂₀₀** was in particular carried out by EXAFS. It consisted in recording and analysing the W L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra of the supported tungsten complexes resulting from the grafting of [WOCl₄] onto SiO₂₋₂₀₀.

The parameters obtained from the fit of the $k^3 \cdot \chi(k)$ EXAFS signal are consistent with the following coordination sphere around W (Figure 2 and Table 1): one oxygen atom at 1.68(1) Å, assigned to an oxo ligand, a bit less than two oxygen atoms (1.7 ± 0.3 O) at 1.87(1) Å, corresponding to σ -bonded siloxy ligands and a bit more than two chloride back-scatterers (2.3 ± 0.3 Cl) at 2.30(1) Å. This is consistent with the bond distances found in [OWCl₂(OAr)₂], type of molecular complexes where the W=O (1.638 - 1.715 Å), W-O (1.831 - 1.978 Å) and W-Cl (2.309 - 2.383 Å) bond lengths are in the same range. Similar W-Cl bond distances have been also observed for crystalline WOCl₄ (2.28 Å for W-Cl; 1.8 Å for W=O) or for molecular complexes where WOCl₄ is bonded to azoxybenzene (2.279 to 2.308 Å for W-Cl; 1.651 to 1.687 Å for W=O) or to a ketone, CF₃C(O)CH=CHNHC₆H₅Br (2.259 to 2.308 Å for W-Cl; 1.664 Å for W=O). Similar parameters were obtained when fitting the $k^2 \cdot \chi(k)$ spectrum. The results thus agree with a major bis-siloxy structure, [(≡SiO)₂WOCl₂], **1a** (70-80%), along with a mono-siloxy species, **1b** (20-30%). This result was supported by NMR of the sample **1*₂₀₀** ([WO*Cl₄] on SiO₂₋₂₀₀), selectively enriched on the oxo moiety by ¹⁷O NMR.

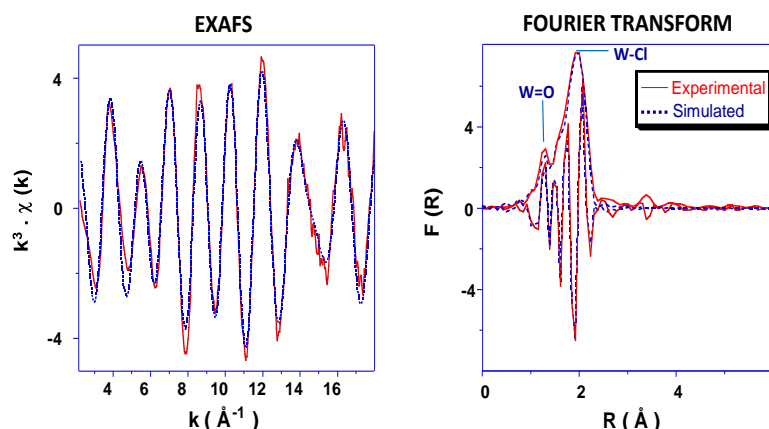


Figure 2. Tungsten L_{III}-edge k^3 -weighted EXAFS (left) and corresponding Fourier transform (right, modulus and imaginary part) with comparison to simulated Sample **1₂₀₀** was further carried out by a XAS study, which consisted in recording and analysing the W L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra of the supported tungsten complexes resulting from the grafting of [WOCl₄] onto SiO₂₋₂₀₀.

Table 1. EXAFS parameters obtained for sample **1₂₀₀**.^a

Type of neighbor	Number of neighbors	Distance (Å)	σ^2 (Å ²)
W=O	1.0	1.68(1)	0.0012(6)
W-OSi≡	1.7(3)	1.87(1)	0.0014(8)
W-Cl	2.3(3) ^b	2.30(1)	0.0036(6)

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. ^a Δk : [2.1-18.0 Å⁻¹] - ΔR : [0.7-2.4 Å]; $S_0^2 = 0.94$; $\Delta E_0 = 9.5 \pm 2.0$ eV (the same for all shells); Fit residue: $\rho = 4.1$ %; Quality factor: $(\Delta\chi^2)/\nu = 3.85$, with $\nu = 11 / 19$. ^b Shell constrained to the parameter above.

EXAFS characterization of sample $\mathbf{1}_{200}$: Further characterization of $\mathbf{2}_{200}$ was carried out by EXAFS. Clearly, when compared to $\mathbf{1}_{200}$, the W-Cl scattering pathway decreases after alkylation (Figure 9). The parameters extracted from the fit of the $k^3 \cdot \chi(k)$ EXAFS spectrum (Table 3) are consistent with one oxo ligand at 1.70(1) Å, ca. two oxygen at 1.88(1) Å and three carbon atoms at 2.12(2) Å, respectively assigned to siloxide and methyl ligands, consistently with the bond distances found in $(\text{SiOx})_2(\text{n-Bu})_2\text{WO}$ (1.705(2) Å for W=O; 1.876 to 1.882 Å for W-O; 2.098 to 2.154 Å for W-C) or in $(\text{O-ArCH}_2\text{N}(\text{Me})\text{CH}_2\text{Ar-O})(\text{Me})_2\text{WO}$ (1.694-1.706 Å for W=O; 1.887 to 1.919 Å for W-O; 2.170 to 2.191 Å for W-C). The W-C distance obtained by EXAFS seems a bit short compared to the last example, however W(O)-Me distances as short as 2.052 Å have already been reported. Similar parameters were obtained when fitting the $k^2 \cdot \chi(k)$ spectrum. Furthermore, the fit was improved when considering a further layer of Cl atom back-scatterers at 2.37(2) Å (only ca. 0.3 such neighbours compared to 2.3 in the starting material), suggesting that the Cl/Me exchange is maybe not fully complete upon reaction with SnMe_4 , and a layer of oxygen back-scatterer at 2.91(4) Å which would be due to oxygen of surface siloxanes of silica. The results obtained are thus in good agreement with a Cl/Me exchange after the reaction of $\mathbf{1}_{200}$ with SnMe_4 leading mainly to $[(\equiv\text{SiO})_2\text{WOMe}_2]$ (**2a**), with most probably $[(\equiv\text{SiO})\text{WOMe}_2\text{Cl}]$ (**2b**) as minor species (ca. 20-30%). This result is in accordance with ^{13}C CP NMR features that indicate the presence of minor W-Me containing species.

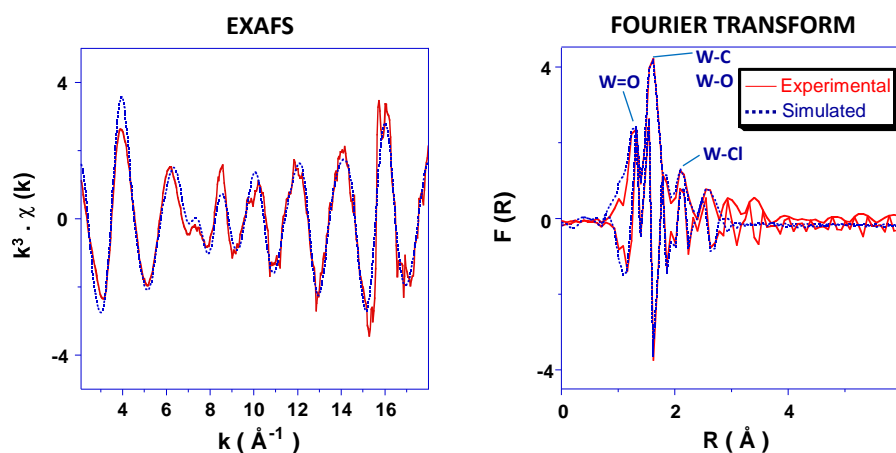


Figure 9. Tungsten L_{III} -edge k^3 -weighted EXAFS (left), for $\mathbf{2}_{200}$ and corresponding Fourier transform (right; modulus and imaginary part). Solid lines: experimental; dashed lines: spherical wave theory.

Table 3. EXAFS parameters obtained for sample $\mathbf{2}_{200}$, resulting from the reaction of $\mathbf{1}_{200}$ with SnMe_4 .^a

Type of neighbor	Number of neighbors	Distance (Å)	σ^2 (Å ²)
W=O	1.0	1.70(1)	0.0017(8)
W-O _{Si}	1.8(2)	1.88(1)	0.0014(5)
W-CH ₃	1.9(4) ^b	2.12(2)	0.006(4)
W-Cl	0.3(2)	2.36(2)	0.002(2)
W-O(Si ₂)	1.0	2.91(3)	0.002(2)

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. ^a Δk : [2.2 - 18.0 Å⁻¹] - ΔR : [0.7-2.9 Å] ([0.7-2.4 Å], when considering only the first coordination sphere without Cl); $S_0^2 = 0.94$; $\Delta E_0 = 8.7 \pm 2.0$ eV (the same for all shells); Fit residue: $\rho = 10.5$ %; Quality factor: $(\Delta\chi)^2/\nu = 3.81$, with $\nu = 11 / 24$ ($[(\Delta\chi)^2/\nu]_1 = 4.99$ with $\nu = 11 / 19$, considering only three backscatterers, oxo, -O and -C in the first coordination sphere of W). ^b Shell constrained to the parameters above and below.