

Evidence for the presence of Mo(vi), W(vi) or Re(vii) species in silica-based materials. New approaches to highly dispersed oxo-species in mesoporous silicates

Jean-Yves Piquemal,^a Emmanuel Briot,^a Maxence Vennat,^a Jean-Marie Brégeault,^{*a} Geneviève Chottard^b and Jean-Marie Manoli^c

^a Systèmes Interfaciaux à l'Echelle Nanométrique, Université de Paris 6 and CNRS-ESA 7069, Case 196, 4 Place Jussieu, F-75252 Paris Cedex 05, France. E-mail: bregeault@ccr.jussieu.fr

^b Chimie des Métaux de Transition, Université de Paris 6 and CNRS-ESA 7071, Case 42, 4 Place Jussieu, F-75252 Paris Cedex 05, France

^c Réactivité de Surface, Université de Paris 6 and CNRS-UMR 7609, Case 178, 4 Place Jussieu, F-75252 Paris Cedex 05, France

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d⁰ Transition metal-containing mesoporous molecular sieves are synthesized by the hydrolysis of tetraethyl orthosilicate in aqueous acid, in the presence of neutral or anionic low-condensed Mo(vi) or W(vi) oxo-peroxo or Re(vii) polyoxo species and a cationic surfactant; the materials have a nearly homogeneous distribution of the dopants and promising catalytic activities.

The recent discovery of mesoporous oxides offers novel possibilities for preparing transition metal-containing materials.¹ Most procedures in acidic (or basic) media require careful control of the rate of hydrolysis of the precursors, *e.g.* alkoxides. In acidic media, with [MoO₄]²⁻, [WO₄]²⁻, *etc.*, large iso-(or hetero-) polyoxometalates (POMs, M = Mo or W) are formed.²⁻⁴ These POMs can be dispersed (or grafted) onto molecular sieves such as MCM-41,⁵ but are not so easily inserted into pure mesoporous silica as they limit wall growth and/or lead to phase segregation. Previous work demonstrates that low-nuclearity neutral or anionic peroxo species can be prepared in 'MO₃/H₂O₂-H₂O-H₃O⁺' precursor systems.^{6,7}

In this work, we consider the electrostatic interaction of these peroxo species with silicate moieties (operating mode A), in the counter-ion-mediated S⁺X⁻I⁺ pathway, as a means of incorporating molybdenum(vi), tungsten(vi) or rhenium(vii) into mesoporous silica. [S⁺ = quaternary ammonium ion surfactant, *e.g.* cetyltrimethylammonium (CTMA⁺); X⁻ = Cl⁻ and/or anionic oxo-peroxo species; I⁺ = inorganic silicate precursor (tetraethyl orthosilicate, TEOS).¹ This procedure is compared with methods involving, or generating, polyoxometalates⁸ or oxo species interacting with TEOS also in the S⁺X⁻I⁺ pathway (operating mode B). The data (Table 1) show that mode A, with Mo or W oxo-peroxo species (run 1, sample A_{Mo}, wt% Mo ≈ 4.05; run 4, sample A_W, wt% W ≈ 7.55) leads to a higher M

content than in the initial gel. On the other hand, with [MeReO(O₂)₂(H₂O)] synthesized from '[Me₃ReO₃]' (denoted MTO)/H₂O₂-H₂O-H₃O⁺ mixtures (run 6, sample A_{Re}, wt% Re ≈ 0.90) the rhenium content is low and a better incorporation can be obtained with aqueous H⁺[ReO₄]⁻ (run 7, sample B_{Re}, wt% Re ≈ 2.5). These results differ from those obtained with basic media (S⁺I⁻ pathway),¹ which correspond to lower loadings of the M species (M = Mo, W or Re) incorporated into the framework of the silica matrix (see, for example, run 3, sample C_{Mo}).

The X-ray data for (Si/M)_{initial} ≈ 50 are similar to those obtained for pure mesoporous silica. Samples A_{Mo}, A_W, A_{Re} and B_{Re} show higher order reflections such as (110), (200), *etc.*, which suggests that they have greater long-range order than samples B_{Mo} and B_W. Because of the relatively low metal content in these materials (Table 1), additional crystalline phases, if any, cannot be identified from the X-ray diffraction patterns, except for (Si/Mo)_{initial} ≤ 30 for example, but some of them can be identified by laser Raman spectroscopy.

This method is very useful for characterizing detemplated materials with Mo or W prepared by the oxo-peroxo (mode A, Table 1) or the oxo-polyoxo route (mode B). Sensitivity to water vapour has been shown by identification of supported H₄[SiMo₁₂O₄₀]. (aq), while in an anhydrous atmosphere, there is no evidence for any crystalline phase or known product (*e.g.* MoO₃). Sample B_{Mo} gives a Raman spectrum corresponding to a mixture of high purity silica MCM-41 and the Keggin unit, 'SiMo₁₂'. The Raman spectra of the W-MCM-41 prepared by the oxo-peroxo route (sample A_W) and by the polyoxo mode (sample B_W) are shown in Fig. 1. They include bands that originate from the SiO₂ matrix [*ca.* 1100, 800 (very weak) and 490 cm⁻¹] as well as from the tungsten oxo species. Bands attributed to the symmetric stretching mode of the terminal

Table 1 Metal (Mo, W or Re) content, interplanar spacing, average pore diameter, wall thickness and BET surface area (S_{BET})^a in mesoporous silicates

Run	Operating Mode with M ^b	Si/M molar ratio			Unit cell parameter a _o /Å	Average pore diameter ^c /Å	Wall thickness ^d /Å	S _{BET} /m ² g ⁻¹
		Gel	Calcined product	d ₁₀₀ spacing/Å				
1	A _{Mo}	50	35	32	37	18	19	1072 ± 60
2	B _{Mo}	50	52	32	37	16	21	1176 ± 60
3	C _{Mo}	50	180	36	41.5	17	24.5	1037 ± 40
4	A _W	50	35	33.5	39	18	21	921 ± 60
5	B _W	50	45	33	38	16	22	897 ± 40
6	A _{Re}	50	300	31.1	36	15	21	1200 ± 60
7	B _{Re}	50	110	31.9	37	16	21	1015 ± 60

^a These parameters refer to the calcined materials. ^bA corresponds to the oxo-peroxo route (S⁺X⁻I⁺ pathway); B to the oxo or polyoxo mode (S⁺X⁻I⁺ pathway); C is typical of synthesis in basic medium with [MoO₂(acac)₂] as the molybdenum(vi) precursor (S⁺I⁻ pathway). ^c Measured by BJH method (desorption). ^d Wall thickness given by the difference between a_o and the average pore diameter.

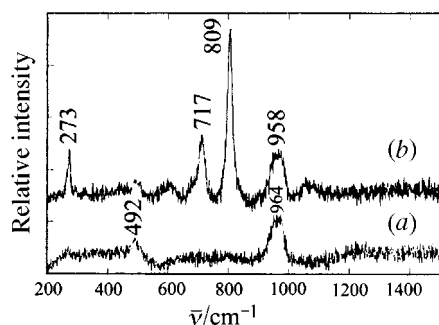


Fig. 1 Raman spectra of mesoporous tungstosilicate [W]-MCM-41; molecular sieves prepared by the oxo-peroxo route (a) and by the oxo-polyoxo mode (b).

W=O bonds are observed at 964 or 958 cm^{-1} . This assignment is still questionable:⁹ terminal Si-O stretching of SiOH...OW 'defective sites' may also contribute. For sample A_W [Fig. 1(a)], no Raman bands due to crystalline WO₃ (*vide infra*) or to 'WO₃·2H₂O'¹⁰ [960 (sharp), 685-662 (broad), 380 and 268 cm^{-1}] are observed. The minor Raman band at 215 cm^{-1} , associated with the W-O-W deformation mode,¹¹ is absent from these spectra but it must be kept in mind that W-O-W linkage can nevertheless exist, since the pore walls of M-MCM-41 resemble amorphous materials rather than crystalline molecular sieves. On the other hand, the Raman spectra of B_W materials, prepared by the aqueous method using ammonium metatungstate, (NH₄)₆[H₂W₁₂O₄₀] or Na₂[WO₄], at ambient temperature and calcined in air at 920 K [Fig. 1(b)], exhibit strong bands due to crystalline WO₃¹⁰⁻¹² at 809, 717 and 273 cm^{-1} , which are assigned to the stretching modes and to the deformation mode (δ) of the O-W-O moieties.¹⁰ The observation of very strong Raman features due to crystalline WO₃ (sample B_W) indicates the formation of a very poorly dispersed SiO₂-supported tungsten oxide phase. Therefore, when the sample is heated, the polytungstate ions transform readily into bulk WO₃ surface species. The achievement of highly dispersed Mo, W and even Re oxo species for these silica-based materials obtained by the aqueous method is attributed to the low nuclearity of the species stabilized by H₂O₂, *e.g.* {MO(O₂)₂ (H₂O)₂}, (M = Mo, W)⁷ or [MeRe(O₂)₂(H₂O)], or more simply by [ReO₄]⁻.

Typical A_{Mo}, A_W, A_{Re} and B_{Re} samples exhibit a reversible, nearly hysteresis-free, type IV isotherm. Nitrogen BET surface areas (Table 1) are in the same range. Desorption hysteresis is not observed for A_{Mo}, A_W, A_{Re} and B_{Re}: a high degree of pore blocking does not occur in these samples but may do so in B_{Mo} and B_W. Mean pore sizes of *ca.* 18 Å (A_{Mo} and A_W) and 16 Å (B_{Mo} and B_W) are found by the BJH method, which is considered to underestimate the real pore size. These values are in fair agreement with TEM measurements, as is the wall thickness (19-22 Å).

X-Ray EDS experiments used to locate and quantify submicroscopic distributions of the Mo, W or Re species reveal that the Mo or W distribution in the typical A_{Mo} or A_W solid is nearly homogeneous; the relative at %Mo[W] being 1.75[2.8] with a difference of 0.7[0.6] between maximum and minimum values.

However, B_{Mo} and B_W have a very inhomogeneous molybdenum or tungsten distribution; the average value is *ca.* 3.0 wt% (B_{Mo}) and values as high as 7.4% are also found, typical differences between maximum and minimum values being 7%. These results compare well with the other data; they indicate that there is a high dispersion or a 'quasi-homogeneous distribution' of the Mo or W sites in samples A, while in samples B there is a less ordered distribution between two (or more) phases as a consequence of phase segregation (*vide supra*).

Syntheses in acidic media would appear to be better than the basic S+I⁻ pathway for the incorporation of M into mesoporous silica. The oxo-peroxo route, for Mo(vi) and W(vi), and the perhenic acid route for Re(vii) in the S+X-I⁺ mediated

pathway are evidently better than synthesis with oxo-polyoxo species in acidic media for obtaining d⁰ metal sites distributed throughout the bulk in spatially uniform states. Even if molybdenum(vi), tungsten(vi) and rhenium(vii) are not statistically and perfectly distributed in the hexagonal cell, high incorporation levels (Si/Mo \approx 35) never achieved before¹ can be obtained with high dispersion of the M species in the framework of the mesoporous materials. Samples A_{Mo} catalyze the oxidation of (*R*)-(+)-limonene with TBHP-decane mixtures (conversion 90%, selectivity to epoxides \geq 98%). Different leaching behaviours are observed as a consequence of the different catalyst preparation methods; they are also related to the nucleophilicity of the reactants and to surface properties. Samples A_M and B_{Re} are also efficient catalysts for oct-1-ene methathesis, some of them without addition of Bu₄Sn or Ph₂SiH₂ cocatalysts. Work is in progress to control these systems better and to optimize epoxidation and metathesis results.

Notes and references

† *Preparation of samples:* A_{Mo} and A_W: MoO₃ (0.36 g, 2.5 mmol) [WO₃·H₂O (0.625 g, 2.5 mmol)] was first reacted with 15 wt% aqueous H₂O₂ (5 ml, 24.5 mmol). After 1 h stirring at 60 °C the solution, denoted A₁, was cooled to room temp. [followed by centrifugation (15 min at 2000 rpm)]. TEOS (\approx 28 ml, 0.125 mol) was mixed with a solution of CTMACl (20 ml, 15 mmol) and 12.5 M HCl (92 ml, 1.15 mol) in H₂O (\approx 220 ml, 17 mol); solution A₁ (Mo or W: 2.5 mmol) was then quickly added. The composition of the gel was: 1 TEOS:0.12 CTMACl:8.9 HCl:136 H₂O:0.19 H₂O₂:0.02 MoO₃. The reaction mixture was stirred (200 rpm) at ambient temperature for 1 h. The pale yellow [white] solid was isolated by filtration, washed with distilled water and dried over P₄O₁₀ to give the initial sample. After efficient drying at room temperature, the powder was calcined in air (200 $\text{cm}^3 \text{min}^{-1}$, 1 K min^{-1}) from ambient temperature to 880-920 K (samples maintained at the final temperature for 4 h) to give sample A_{Mo} [A_W].

B_{Mo} and B_W: syntheses were adapted from methods previously described¹³ for (Si/Mo)_{initial} \approx 100 mol/mol. To a solution of CTMACl (7.3 g, 0.02 mol) and 12.5 M HCl (8 ml, 0.1 mol) in H₂O (270 ml, 15 mol) were added precursor K₂MoO₄ (0.48 g, 2 mmol) [Na₂WO₄ (0.59 g, 2 mmol)] and TEOS (22.3 ml, 0.1 mol). The reaction mixture was stirred vigorously at ambient temperature for 24 h, then filtered, washed and treated as above for A_{Mo} and A_W.

A_{Re} and B_{Re}: MTO was prepared by a slightly modified version of the published method¹⁴ starting from 10 g of Re₂O₇ in an overall yield of 85% after silica gel chromatography and recrystallization. HReO₄ was prepared from H₂O₂ (30% m/v) and metallic rhenium. A_{Re} and B_{Re} were prepared by a modification of the A_{Mo}, A_W and B_{Mo}, B_W pathways.

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