

Cite this: *Chem. Commun.*, 2011, **47**, 4285–4287

www.rsc.org/chemcomm

An easily accessible Re-based catalyst for the selective conversion of methanol: evidence for an unprecedented active site structure through combined *operando* techniques†

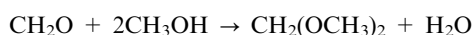
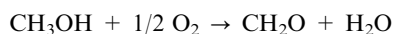
Anthony Yoboué,^{ab} Audrey Susset,^{ab} Asma Tougerti,^{ab} Daniel Gallego,^{ab}
Sudarsan Venkat Ramani,^{ab} Malathi Kalyanikar,^{ab} Dmitriy S. Dolzhenkov,^{ab}
Sileshi G. Wubshet,^{ab} Yilun Wang,^{ab} Sylvain Cristol,^{ab} Valérie Briois,^{cd} Camille La Fontaine,^c
Régis. M. Gauvin,^{abd} Jean-François Paul^{ab} and Elise Berrier^{*abd}

Received 13th December 2010, Accepted 8th February 2011

DOI: 10.1039/c0cc05542e

Heterogeneous Re/SiO₂ catalysts prepared using a one pot sol–gel synthesis were found to display high activity in the direct, selective methanol conversion to methylal, which is correlated to an unprecedented rhenium oxide structure.

The direct conversion of alcohols over heterogeneous catalysts affords a most strategic entry to valuable chemicals from biomass. Besides its potential application for green chemistry, this reaction is also a remarkable model for probing both the redox and acidic functions of a given catalyst.^{1,2} In particular, the direct conversion of methanol to dimethoxymethane (DMM or methylal) involves the oxidation of methanol to formaldehyde and subsequent condensation of two methanol molecules with formaldehyde:



The reaction pathway requires a bifunctional catalyst retaining at least one mild redox couple to oxidise the methanol to formaldehyde with no further oxidation to CO_x, and one acidic function (Lewis or Brønsted type) to mediate the condensation reaction. Thus the balance between those two functions on the catalyst must be tuned to orientate the selectivity towards the targeted DMM. Supported or bulk rhenium oxide-based materials were first identified by Iwasawa *et al.* as efficient catalysts for the direct conversion of methanol to DMM.^{3,4} Indeed, Re_xO_y oxides possess the right redox/Lewis acidity

balance to perform the direct conversion of methanol to DMM under mild conditions without needing further modification. The efficiency of those rhenium-based catalysts was ascribed to the Re⁶⁻⁷⁺/Re⁴⁺ redox potential coupled with an appropriate Lewis acidity of rhenium oxide.³

Up to now, neither the preparation technique nor the support nature was found to exert significant influence on the structure of the ReO_x phase. The latter is generally depicted as mainly retaining isolated ReO₄ moieties featuring a distorted tetrahedral coordinated mode.⁵ Under hydrated conditions, the oxorhenate phase is alike free perrhenate anion, ReO₄⁻, which is the only existing structure of aqueous rhenium oxide, regardless the pH of the solution. On the basis of thorough *in situ* studies, Lee and Wachs have recently concluded on the structure of Re/SiO₂ materials. According to their findings, under dehydrated conditions, the ReO_x structure is consistent with isolated tri-oxo species, Si–O–Re(=O)₃, responsible for Raman bands at 343, 977 and 1010 cm⁻¹, respectively assigned to δ(O–Re–O), ν_{as}(Re=O) and ν_s(Re=O) modes.^{6,7} This structure was also evidenced by Lacheen *et al.* for Re/H-MFI materials prepared using a grafting procedure in strict absence of water.⁸ Although it was initially proposed that rhenium oxide is present as dimeric Re₂O₇ species in ZSM-5, the same isolated ReO₄ structure was subsequently concluded to be present.

On the other hand, regarding catalytic performances, the nature of the support was reported to strongly alter both the selectivity and the conversion levels. This was previously assigned to the support-induced reducibility of the oxorhenate phase⁹ as well as the intrinsic acidity of the support.¹⁰ In particular, ReO_x/SiO₂ materials prepared using classical preparation techniques (incipient wetness impregnation or chemical vapour deposition) were depicted as poor catalysts for methanol conversion to methylal:^{4,10,11} the conversion level is low and significant amounts of methyl formate and CO₂ are produced along with DMM, revealing an undue redox capability of the oxorhenate phase.

Thus, the design of novel catalytic materials for a reaction of such a wide importance will stem from adequate tuning of

^a Université Lille-Nord de France, 59000 Lille, France

^b Unité de Catalyse et de Chimie du Solide, Bât. C3 Cité Scientifique Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France.

E-mail: Elise.Berrier@univ-lille1.fr; Fax: +33 3 20 45 65 61; Tel: +33 3 20 43 49 47

^c SAMBA Beamline, Synchrotron SOLEIL, Saint Aubin, 91190 Gif s/ Yvette, France

^d CNRS, Centre National de la Recherche Scientifique, France

† Electronic supplementary information (ESI) available: Characterization of the pure SiO₂ support; compared TPR profile of 10ReSi and 10%ReO_x/Aerosil 200; procedure for catalytic test; EXAFS procedure. See DOI: 10.1039/c0cc05542e

the metal–support partners' features, and will require deep understanding prior to further improvement. In this communication, a simple, new preparation based on the gelification of a sol containing a silica precursor together with perrhenic acid is presented. The addition of an acidic salt is known to strongly alter the structure and reduce the porosity of a silica gel.¹² Hence, this one-pot procedure is expected not only to lessen rhenium volatilization, but also to generate local environment(s) around the metal that would feature original metal–support interactions.

To 20 mL of a solution of tetraethyl orthosilicate (Aldrich) in ethanol (20 mL) a solution of perrhenic acid (0.15 M) in water (20 mL) was added dropwise under vigorous stirring at 65 °C. The mixture was continuously stirred at 65 °C until gelation, which occurred 9 hours after water introduction. The gel, a light-pink powder, was dried in air at 120 °C overnight. During this step, the powder turned to light brown. This dry gel was introduced in a reactor and heated under an O₂/He mixture (50%–50%) up to 400 °C (6 hours dwell time) to remove the organics and stabilize the oxorhenate structure. The resulting material, a white powder, effectively retains 10.5%_{wt} Re and will be further denoted as **10ReSi**. As investigated using N₂ equilibrium adsorption, the pure SiO₂ support, prepared accordingly, exhibits a Langmuir-like adsorption isotherm featuring micropores, exclusively.†

The catalytic performances of **10ReSi** in the oxidation of methanol were then probed in a flow reactor (Table 1).

After one hour on stream, the yield in DMM reaches 36%_{mol} at 240 °C and 29%_{mol} at 260 °C. As a comparison, the typically reported yields for Re/SiO₂ catalysts operating conversion of methanol to methylal are 9%_{mol} at 240 °C³ and 4%_{mol} at 260 °C.⁹ The decrease of the conversion level when increasing the temperature from 240 to 260 °C is assigned to rhenium volatilization. At 150 °C, almost only DME is produced: this indicates that the acidic function of the catalyst operates at mild temperatures while the redox capability is activated in the 200–240 °C range. No loss of acidic strength is reported as the formaldehyde production remains marginal for all temperatures. In comparison with standard ReO_x/SiO₂ and, more generally, acetalization catalysts, unique levels for both methanol conversion and selectivity in methylal were measured. Remarkably, the one pot preparation described here induced a significant decrease of the rhenium redox potential and favoured the DMM production once the temperature is high enough to activate the reduction of Re⁷⁺. Indeed, the reduction of **10ReSi** by H₂ was found to

Table 1 Catalytic properties of **10ReSi** in CH₃OH oxidation†

Temp./ °C	Conversion ^a (% _{mol})	Selectivities (% _{mol})				
		DMM	DME	MF	F	CO _x
150	15.5	0	98	0	2	0
200	20	35.5	62.7	0	0.5	1.3
240	40.6	89.1	6.0	2.2	0.8	1.9
260	31.8	91.6	3.5	2.4	0.3	2.2

Experimental conditions: CH₃OH 4.7%, O₂/CH₃OH 1:2. GHSV: 26000 mL h⁻¹ g_{cat}⁻¹, 1030 h Pa.^a After one hour on stream. DME: dimethyl ether, MF: methyl formate, F: formaldehyde; DMM: dimethoxymethane.

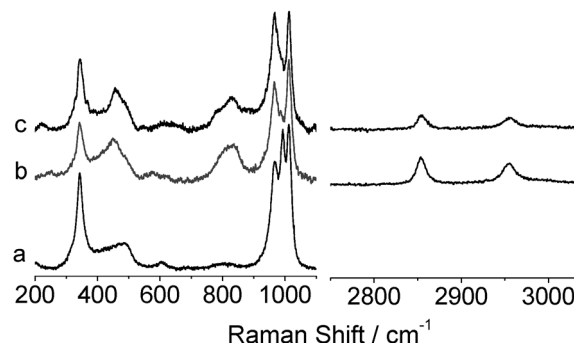


Fig. 1 Operando Raman spectra of **10ReSi**: (a) under O₂, at 350 °C prior to methanol introduction, (b) after 45 minutes under CH₃OH/He/O₂ at 200 °C, (c) after reaction, flushed with O₂ for 10 min.

occur at temperatures exceeding 400 °C while the one observed for a model 10% ReO_x catalyst supported onto Aerosil 200¹⁰ reached 280 °C.†

A structural investigation was carried out using operando Raman and X-ray absorption spectroscopies. The Raman spectra of **10ReSi** before, during and after the reaction are presented in Fig. 1.

The silica support gives rise to broad Raman features visible at 500 (ω_1), 600 (D₂) and 800 cm⁻¹ in the spectrum of **10ReSi** (Fig. 1a).¹³ Intense Raman stretching ν (ReO) modes in the oxorhenate phase are also observed at 968, 992 and 1012 cm⁻¹ together with a shoulder at 944 cm⁻¹.† As previously reported, the δ (OReO) mode is responsible for a broad band at 343 cm⁻¹ while the bands at 968 and 1012 cm⁻¹ are assigned to dehydrated isolated tri-oxo moieties,⁶ further designated as **ReOx-a**. On the other hand, the modes at 944 and 992 cm⁻¹ were never described in the literature so far under such conditions and are assignable to an unprecedented structure of supported rhenium oxide, presently denoted as **ReOx-b**. Under reaction conditions at 200 °C (Fig. 1b), the band previously observed at 992 cm⁻¹ is shifted to 986 cm⁻¹. The relative contribution of the band at 343 cm⁻¹ is lowered while new bands centred at 830 (broad), 447 and 248 cm⁻¹ (weak) are observed. Interestingly, the frequencies of the ν (Re=O) modes at 968 and 1012 cm⁻¹ are absolutely not shifted to lower frequencies under reaction conditions, contrary to what was previously stated in many active systems based on supported oxides.¹⁴ This trend is in line with the reported poor activity of **ReOx**-moieties, the only structure for ReO_x/SiO₂ catalysts described so far. On the other hand, the new structure evidenced in the present work is modified, which pleads in favour of **ReOx-b** being the active phase. After one hour on stream, the catalyst was flushed 10 min under He and another 10 min under pure O₂ at 200 °C. This step did not lead to significant changes in its Raman spectrum compared to the one recorded under working conditions (Fig. 1c). Indeed, a further heating up to 220 °C under pure O₂ was necessary to recover the initial spectral features. The bands at 2854 and 2955 cm⁻¹ observed under CH₃OH flow are still present. This trend is consistent with a particularly strong adsorption of CH₃O-groups onto the silica surface.¹⁵

As Raman analysis points at a correlation between the enhanced catalytic activity and the original **ReOx-b** structure, *in situ* XAS investigations were carried out in order to provide further information. The XANES spectrum of **10ReSi** recorded

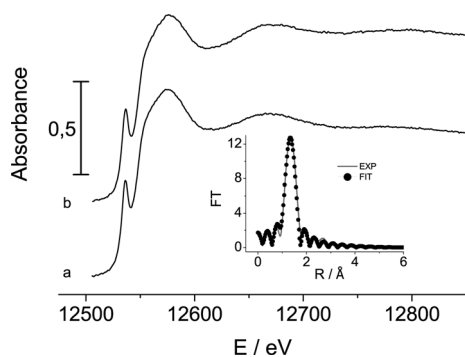


Fig. 2 (a) Experimental XANES spectrum of **10ReSi**, O₂, 350 °C and (b) experimental XANES spectrum of solvated ReO₄⁻ in water (aqueous perrhenic acid); in inset: Fourier transform of the EXAFS signal. XANES and EXAFS spectra were recorded at the Re L_I edge and Re L_{III} edge, respectively, on SAMBA Beamline, SOLEIL in Qu-EXAFS configuration.^{†16}

at 350 °C under O₂ flow, shown in Fig. 2a, is essentially similar to that of perrhenic acid in aqueous solution (Fig. 2b).

The presence of a pre-edge peak of high intensity indicates that the rhenium atom stands as Re^{VII} in tetrahedral coordination. This is confirmed by the analysis of the first shell of the EXAFS spectrum as it can be fitted with 4 oxygen neighbours. No contribution from neighbouring Re is visible in the Fourier transform of the EXAFS spectrum (in inset, Fig. 2), indicating that ReO_x moieties are essentially isolated.¹⁷ As a consequence, the new **ReOx-b** structure evidenced by Raman spectroscopy is not consistent with Re oligomers.

The Raman frequencies and the wet pathway chemistry used for the preparation make a peculiar interaction of the oxorhenate phase with water possible. An *in situ* Raman investigation of the gradual hydration of **10ReSi** at 175 °C was thus run to clarify this point (Fig. 3).

Upon hydration, the relative contribution of the **ReOx-b** form is increased at the expense of the **ReOx-a** one. Additional broad features are also detected around 800 and 850 cm⁻¹ (Fig. 3, 1 to 120 min). A further hydration led to the formation of free perrhenate anion characterized by a band at 972 cm⁻¹ ($\nu_S(\text{Re}=\text{O})$) and a shoulder at 920 cm⁻¹ ($\nu_{AS}(\text{Re}=\text{O})$) in Fig. 3 (top). The increase of the contribution of the **ReOx-b** form with increasing the water content strongly supports that this new species is related to partly hydrated ReO_x species which are not free perrhenate anion (920, 970 cm⁻¹). Interestingly,

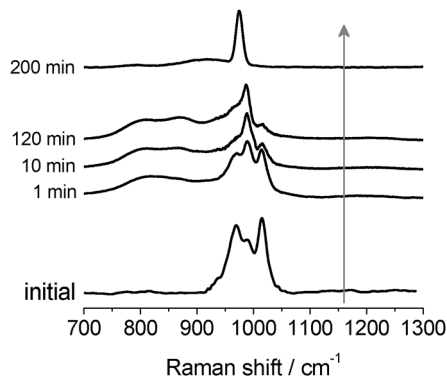


Fig. 3 *In situ* Raman spectra of **10ReSi** (A) recorded along its controlled hydration under 15% H₂O in He at 175 °C.

the hydration process is reversible: we could observe both the **ReOx-b** and **ReOx-a** forms by dehydrating the material again. Precedent to such species exist in the literature, as for instance in the case of [Re₂O₇(H₂O)₂] that features two rhenium-coordinated water molecules, as shown by X-ray diffraction studies.¹⁸ Most interestingly, as in the **10ReSi** case, further hydration of this compound leads to formation of aqueous perrhenic acid. This hypothesis is not contradictory with the XAS data, in so far as a weak interaction with water is not expected to modify the XANES nor the EXAFS spectra, especially when the structure remains disordered.¹⁷ Other structures implying silanols or specific sites of silica gel (cyclic structures, as an example) may also be considered.

In conclusion, our new ReO_x/SiO₂ catalyst prepared using a unique sol-gel wet route exhibits a markedly lower redox potential that finely tunes the redox/acidic properties towards highly efficient and selective conversion of methanol into DMM. Most interestingly, these features have been correlated to the observation of an unprecedented structure in which the ReO₄ tetrahedron is in weak interaction with water. Our current investigations are targeted at the determination of the actual structure of this new form of supported rhenium oxide, an intermediate between fully dehydrated ≡Si-OReO₃ and aqueous ReO₄⁻ anion.

The work was supported by the ANR SAXO project (Grant number ANR-07-BLAN-0265-01). We thank the Ministry of Higher Education and Research (PhD grant for AY) and the CNRS for financial support.

Notes and references

- 1 J.-M. Tatibouët, *Appl. Catal., A*, 1997, **148**, 213.
- 2 M. Badlani and I. E. Wachs, *Catal. Lett.*, 2001, **75**(3–4), 137.
- 3 Y. Yuan, T. Shido and Y. Iwasawa, *Chem. Commun.*, 2000, 1421; Y. Yuan, K. Tsai, H. Liu and Y. Iwasawa, *Top. Catal.*, 2003, **22**, 9.
- 4 Y. Yuan, T. Shido and Y. Iwasawa, *J. Phys. Chem. B*, 2005, **109**, 2155.
- 5 B. Mitra, X. Gao, I. E. Wachs, A. M. Hirt and G. Deo, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1144–1152.
- 6 E. L. Lee and I. E. Wachs, *J. Phys. Chem. C*, 2008, **112**, 6487; E. L. Lee and I. E. Wachs, *J. Phys. Chem. C*, 2007, **111**, 14410.
- 7 J. Okal and J. Baran, *J. Catal.*, 2001, **203**, 466–476.
- 8 H. S. Lacheen, P. J. Cordeiro and E. Iglesia, *J. Am. Chem. Soc.*, 2006, **128**, 15082; H. S. Lacheen, P. J. Cordeiro and E. Iglesia, *Chem.–Eur. J.*, 2007, **13**, 3048.
- 9 R. M. Edreva-Kardjeva and A. A. Andreev, *J. Mol. Catal.*, 1988, **46**, 201.
- 10 Y. Fu and J. Shen, *Chem. Commun.*, 2007, 2172; Q. Sun, J. Liu, J. Cai, Y. Fu and J. Shen, *Catal. Commun.*, 2009, **11**, 47.
- 11 X. Sécordel, A. Yoboué, E. Berrier, S. Cristol, C. Lancelot, M. Capron and J.-F. Paul, *J. Solid State Chem.*, 2010, accepted.
- 12 E. Berrier, L. Courtheoux, M. Bouazaoui, B. Capoen and S. Turrell, *Phys. Chem. Chem. Phys.*, 2010, **12**(43), 14477–14484.
- 13 F. L. Galeener, R. A. Barrio, E. Martinez and R. J. Elliot, *Phys. Rev. Lett.*, 1984, **53**, 2429–2432.
- 14 J. M. Jehng, H. Hu, X. Gao and I. E. Wachs, *Catal. Today*, 1996, **28**, 335–350; M. A. Bañares, in *In situ Spectroscopy of Catalysts*, ed. B. M. Weckhuysen, ASP, 85, 2004; W. Zhang and S. Ted Oyama, *J. Phys. Chem.*, 1996, **100**, 10759–10767.
- 15 D. S. Kim, M. Ostromecki, I. E. Wachs, S. D. Kohler and J. G. Ekerdt, *Catal. Lett.*, 1995, **33**(3–4), 209–215.
- 16 V. Briois, E. Fonda, S. Belin, L. Barthe, M. Rubbens, F. Villain and C. La Fontaine, *accepted to Uvx*, 2010, DOI: 10.1051/UVX/2010002, EDP Sciences.
- 17 A. Tougerti, S. Cristol, E. Berrier, V. Briois, C. La Fontaine, F. Villain and Y. Joly, *in preparation*.
- 18 C. C. Romao, F. E. Kühn and W. A. Hermann, *Chem. Rev.*, 1997, **97**, 3197–3246.