Electronic Supplementary Material (ESI) for Chemical Communications

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

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Electronic Supplementary Information

Characterization of the pure SiO_2 support

Compared TPR profile of 10ReSi and 10%ReO_x/Aerosil200

Procedure for Catalytic Test

Decomposition of the Raman spectrum of 10-ReSi

EXAFS data acquisition

Characterization of the pure SiO_2 support prepared by sol-gel and calcined at 400°C

A sample of pure silica was prepared using the very same procedure as the 10ReSi catalyst. The adsorption isotherm features a typical Type I (Langmuir) isotherm. The porosity is completely saturated for a partial pressure as low as 0.2, indicating the solid features micropores. In the present case, the Langmuir equation is more suitable than the BET one since the adsorption is restricted to monolayer.

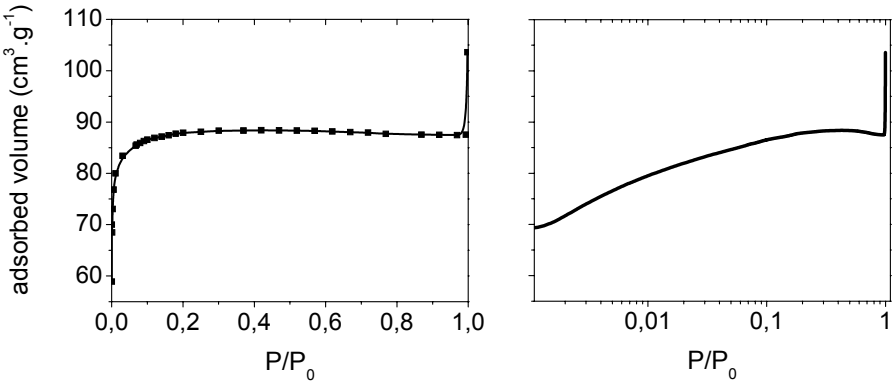

Figure SI-1: N_2 adsorption isotherm of pure silica prepared using the sol-gel procedure and calcined at 400°C for 6 hours under He/O_2 (50:50) flow

Compared TPR profile of 10ReSi and 10%ReO_x/Aerosil200

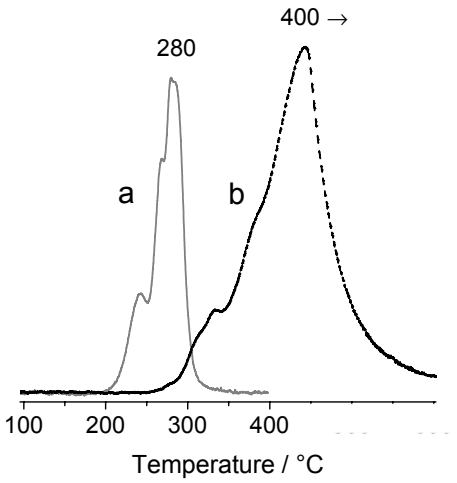

Figure SI-2: H_2-TPR profile of a) 10%ReO_x/SiO_2-Aerosil and b) 10ReSi catalysts

Procedure for Catalytic Test

The operating conditions for the catalytic test were the following: CH_3OH 4.7%$_{mol}$ in He, O_2 9.8%$_{mol}$, total flow measured: 21.4 mL.min^{-1}; GHSV: 26,000 mL.h^{-1}.g$_{cat}$$^{-1}$, atmospheric pressure (1025-1035 hPa). The methanol was introduced by bubbling He in a saturator equipped with a condenser to set the vapour temperature and tune the methanol content.

Decomposition of the Raman spectrum of 10-ReSi

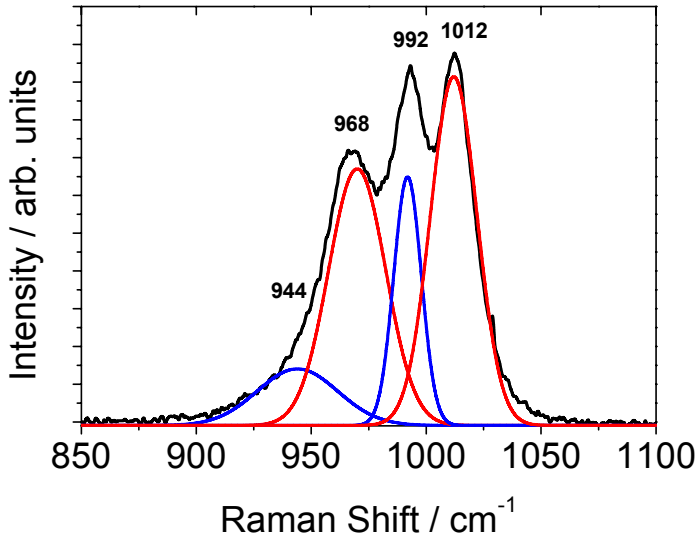

Figure SI-3: Proposition for decomposing the Raman spectrum of 10-ReSi into Gauss curves

EXAFS data acquisition

The operando XAS was carried out at SOLEIL on the SAMBA beamline (Spectroscopies Applied to Materials Based on Absorption) in its Qu-EXAFS (Quick-EXAFS) operating mode[1]. The bending magnet radiation from the SOLEIL source was vertically collimated by a first cylindrical bent mirror onto a Si(111) channel cut mounted on a cam driven tilt table allowing it to oscillate periodically with amplitude

1 [1] V. Briois, E. Fonda, S. Belin, L. Barthe, M. Rubbens, F. Villain, C. La Fontaine, *accepted to UVx 2010,* **DOI 10.1051/UVx/2010002**, EDP Sciences
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$\Delta\theta(t)$ around an average fixed Bragg angle, θ_B. This amplitude can be tuned from 0.1 to 4° by an original SOLEIL in vacuum variable cam design. The θ_B Bragg angle was set to 10.894374 ° and the oscillation frequency was 1 Hz. The amplitude oscillation was 2.27°, which allowed a simultaneous collection of absorption spectra at Re L_{123} edges. A second cylindrical bent mirror focused the monochromatic beam at the sample position. The size of the beam is approximately 4000 (H) x 500 (V) μm^2. The X-rays grazing incidence of the mirrors was set at 4 mrad in order to reject harmonics. XAS data were collected under working conditions in transmission mode using ionization chambers. Typically 300 scans (5 minutes acquisitions) were averaged in order to get an acceptable signal-to-noise ratio.

EXAFS fit parameters

EXAFS fitting results of the 10ReSi sample:

Sample	Path	N (coordination)	R(Å)	ΔE_0 (eV)	σ^2	R-factor
10ReSi	Re-O	4.2	1.73	0.28	0.003	2.810^{-3}