Cell for the *in situ* study of heterogeneous catalysts by transmission and fluorescence XAS spectroscopy

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A simple cell, assembled with commercial parts, suitable for *in situ* X-ray-absorption spectroscopy measurements of heterogeneous catalysts, has been designed. The cell, light and easy to handle, allows thermal treatments of the sample under investigation up to 823 K in a reducing or oxidizing atmosphere and measurements at both high and liquid-nitrogen temperature. The cell was tested by studying the decomposition, in an oxygen flow, of ammonium metatungstate to WO_3. Extended X-ray absorption fine-structure measurements of the ammonium metatungstate before and after a thermal treatment at 773 K are reported.

Keywords: $(NH_4)_6H_2W_{12}O_{40}$; ammonium metatungstate; WO_3; X-ray absorption spectroscopy; heterogeneous catalysis.

1. Introduction

The interest in the application of X-ray absorption spectroscopy (XAS) to the study of heterogeneous catalysts has remarkably increased in the past few years (Vaarkamp & Koningsberger, 1997) because this technique determines the local structure of the surface active species. However, in order to obtain a useful description the catalyst must be investigated under reaction conditions and *in situ* experiments are often necessary. These require a specially equipped cell because, during the activation process or catalytic reaction, the sample under investigation must be heated in a vacuum or in a controlled atmosphere. During the extended X-ray absorption fine-structure (EXAFS) measurements the temperature of the sample should be lowered to 77 K in order to reduce thermal disorder in the local structure. The cell must be light enough for easy transportation and handling. Several cells have been described in the literature (Kampers *et al.*, 1989; Zhang *et al.*, 1991; Bazin *et al.*, 1996; Dalla Betta *et al.*, 1984; Lytle *et al.*, 1985; Neils & Burlitch, 1989). Their construction appears quite complex and expensive as, for their assemblage, many parts have been specially manufactured. In the present paper we describe a simple light and handy *in situ* cell, assembled mostly with commercial parts. The cell allows thermal treatments up to 823 K in a reducing or oxidizing atmosphere and may be used for measuring X-ray absorption spectra in the transmission and fluorescence modes at both high and low temperature.

As our research interest aims to characterize tungsten species supported on zirconia, prepared by dispersion of ammonium metatungstate $[(NH_4)_6H_2W_{12}O_{40}]$ and subsequent thermal treatment in an oxygen atmosphere, the study of the pure tungsten compound was a prerequisite.
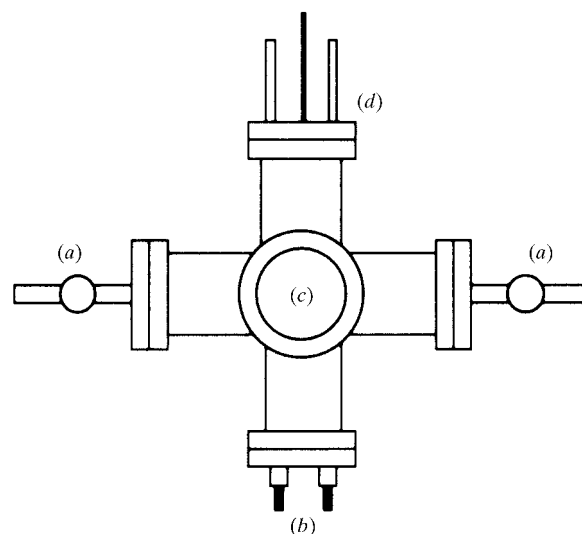

Figure 1
Front view of the EXAFS cell in the transmission mode [the short arm is not visible because it is on the opposite side with respect to (*c*), behind the drawing plane]. (*a*) Stopcocks for the gas inlet, outlet and/or vacuum connection. (*b*) Flange of the heater. (*c*) Kapton windows. (*d*) Sample holder flange.

The purpose of the present investigation was therefore twofold: to test the cell and to study the *in situ* decomposition of ammonium metatungstate to tungsten trioxide (WO$_3$).

2. Cell description

The cell (Fig. 1) was devised for use at the ESRF Gilda beamline and consists of a stainless steel six-way cross (from Caburn MDC, CX6-40) having five arms of equal length (63 mm) and one shorter arm (40 mm). The latter was necessary to fit the cell into the beamline chamber in the presence of the fluorescence detector. The arms (36 mm in internal diameter) are closed with flanges (Caburn MDC, DN40 CF), three of which are rotatable and have different functions. Two flanges are bored (30 mm in diameter) and equipped with 30 mm-thick epoxy-sealed kapton windows for the ingoing and outgoing radiation. Two other flanges are equipped with a tube and stopcock each for the gas inlet and outlet or for a vacuum pump connection. One of the remaining two flanges carries the heater, the other carries the sample holder.

The heater consists of two silica cylinders, 60 mm long, 22 and 36 mm in external diameter (Fig. 2). Three holes (10 mm in diameter), two at 180° and the third at 90° drilled half-way down the cylinder, allow transmission and fluorescence measurements. The internal silica cylinder has a double coil of Ni/Cr wire (0.4 mm in diameter), electrically insulated with a ceramic fibre ribbon. The external coil is taped with a layer of the same insulating material and the ensemble is gently put into the external silica cylinder so that the holes of the internal and external cylinders correspond. The ends of the wire are clamped to a power feedthrough (Caburn HV-25C-2-C40). At room temperature the heater has a total resistance of 20 Ω.

The sample holder is made of brass and has a hole (10 mm in diameter) for the sample pellet (Fig. 3). To improve its thermal contact the sample is gently pressed with a clamp. To cool the sample during measurement the sample holder is welded to a stainless-steel U-shaped tube (4 mm in external diameter) for liquid nitrogen flow. The ends of the U-shaped tube are welded to two wider tubes (6 mm in external diameter) that cross the flange and are fitted with two Swagelok fittings. A Chromel-Alumel thermocouple (Tersid MTS-40l63), inserted into the cell by a feedthrough crossing the flange and sited in an appropriate hole on the sample holder, monitors the sample temperature and provides feedback to the thermoregulator. The cell is installed into the beamline chamber by two steel bars connected to a flange (DNl60 ISO LF) having Swagelok fittings for liquid nitrogen supply and the thermocouple. This flange is linked to bellows that allow the cell to move freely in all directions, thus making it easier to find the best position for the sample.

Although the cell can be employed for measurements both in the transmission and in the fluorescence mode, only transmission spectra have been collected for the present work. Measurements in the fluorescence mode have been carried out on different samples not discussed in the present paper. Transmission and fluorescence measurements require different configurations of the flanges with the kapton windows. For transmission they must simply be placed along the radiation path with the samples inserted between them. For fluorescence they must be placed at 90° by exchanging the position of the outgoing window with that of the gas inlet or outlet. The outgoing radiation window must be located on the short arm of the six-way cross close to face the fluorescence detector. In addition, the sample holder flange must be rotated at a 45° angle to allow the fluorescent radiation to be collected onto the detector. The detector was a silicon photodiode which collects all of the radiation diffused from both the sample and the steel cell. However, the geometry of the apparatus is properly set so that the sample absorbs a great part of the incident beam, and that the radiation diffused from the cell and reflected just onto the detector is negligible. In fact, in the whole energy range, our XAS spectra do not show any change in the slope which is characteristic of a background effect due to the radiation diffused from the cell.
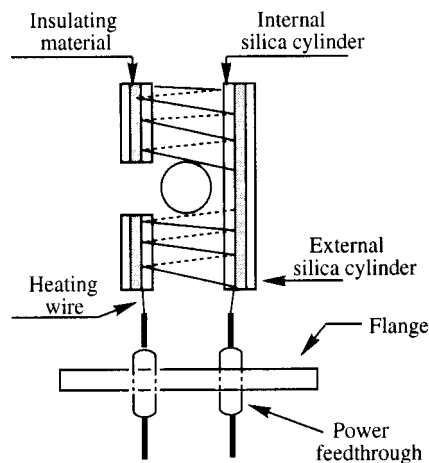

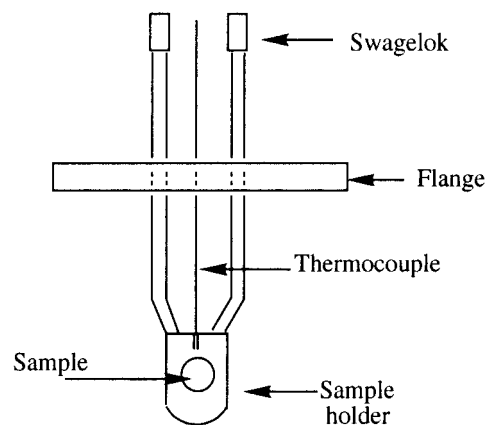**Figure 2**
Schematic drawing of the heater.

Figure 3
Schematic drawing of the sample holder.

No matter how the flanges are arranged, the sample can be changed simply by unscrewing the upper flange of the *in situ* cell and lowering the cell.

3. Experimental

3.1. *Cell tests*

The cell proved to be vacuum tight having been tested up to 13 μPa. It also proved gas tight up to the p.p.m. level when operated under atmospheric pressure. The test was performed by placing the cell containing He at atmospheric pressure into a container that could be evacuated. The residual gas in the container was then analysed with a mass spectrometer. As we are interested in using the cell for treating samples in an oxygen atmosphere, the sample temperature was calibrated while flowing oxygen (3 cm^3 min^{-1}) in the cell. Three Chromel-Alumel thermocouples were used: the first on the sample holder to monitor the temperature for the power supply control, the second dipped into the sample pellet, and the third clamped to the flange on the shorter arm to monitor the kapton window temperature. For calibration at temperature higher than room temperature, a power supply, equipped with a proportional thermoregulator, was set to obtain a given sample holder temperature. After 3 min, equilibrium was reached and the temperatures of both the sample and the sample holder were recorded. The procedure was repeated increasing the sample holder temperature in steps of 100 K. During the heating the cell was in air. At the highest temperature reached on the sample holder, 823 K, the pellet temperature was 50 K less than that of the sample holder and the maximum temperature at the flange was 348 K. It was verified that these temperature values were stable during a period of time of ~2 h. No higher temperatures were tested to avoid failure of the heating resistance. However, the heating resistance can be easily built to meet the desired performance. Obviously for much 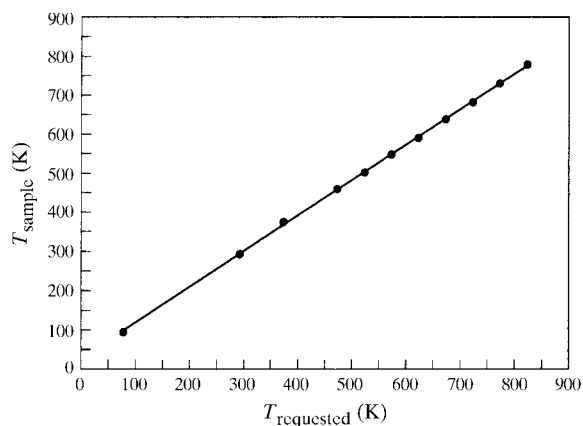higher temperatures a cooling system could be necessary to avoid the overheating of the kapton windows. The calibration below room temperature was carried out while cooling the cell under liquid nitrogen flow. The lowest temperature at the sample thermocouple, 94 K, was reached in 10 min and was stable. The calibration temperature curve is shown in Fig. 4.

3.2. *EXAFS measurements*

Tungsten L_{III}-edge EXAFS spectra were measured at the liquid nitrogen temperature, in the transmission mode, with a Si(311) double-crystal monochromator.

A pellet of ammonium metatungstate mixed with boron nitride (BN) (Fluka) was prepared while powders of commercial WO_3 (Schuchardt) and Na_2WO_4, used as reference compounds, were deposited on millipore membranes and then packed into adhesive kapton. As for ammonium metatungstate, data were collected before and after heating. For thermal treatment the sample was heated *in situ* up to 773 K, keeping this temperature constant for 1 h in a dry oxygen flow. Data were analysed by using the Michalowicz set of programs (Michalowicz, 1990). After extraction, the EXAFS signals were filtered and the Fourier transforms (FT) of the $\chi(k)k^2$ signals were calculated in the 2.5–12.0 Å^{-1} k-space interval with a Kaiser window. The 12.0 Å^{-1} upper limit for the FT was chosen because the spectrum of the ammonium metatungstate sample does not show a great residual signal at higher k values.

The analysis of the first coordination shell was performed by inverse FT and by curve-fitting of the obtained signals in the single-scattering approximation. Distances (R_j), coordination numbers (N_j) and Debye–Waller factors ($\Delta\sigma_j^2$) are reported in Table 1. The tungsten–oxygen phase shift and backscattering amplitude used for fitting were extracted from the peak in the FT of sodium tungstate, which represents the first oxygen shell with $R_1 = 1.819 \pm 0.008$ Å and $N_1 = 4$ (Okada *et al.*, 1974).

Figure 4
Temperature of the sample *versus* requested temperature, measured in an oxygen flow at 3 cm^3 min^{-1} using a proportional thermoregulator.
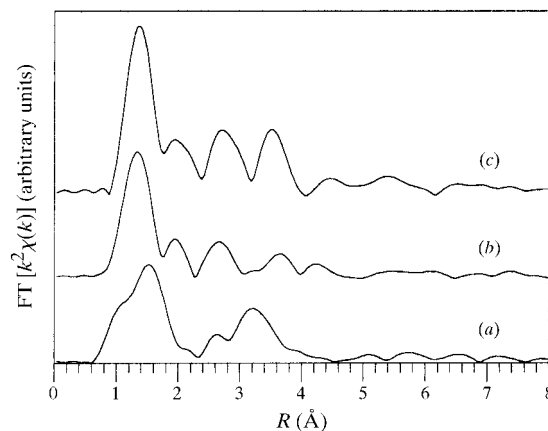
Figure 5
Fourier transform of EXAFS (without phase correction) for (*a*) ammonium metatungstate before thermal treatment, (*b*) the sample in (*a*) after *in situ* decomposition at 773 K in a dry oxygen flow, (*c*) commercial WO_3.

Table 1
The best-fit EXAFS results and neutron diffraction results (Loopstra & Boldrini, 1966).

N: coordination number; *R*: bond length; $\Delta\sigma^2$: Debye-Waller factor.

Compound	N (± 0.5)	R (± 0.02) (Å)	$\Delta\sigma^2$ ($\pm 1 \times 10^{-3}$) (Å^2)
Ammonium metatungstate	0.6	1.72	4.0×10^{-4}
	4.0	1.93	4.0×10^{-4}
	1.0	2.18	1.0×10^{-4}
In situ treated	1.2	1.79	9.0×10^{-3}
	2.1	1.87	8.0×10^{-3}
	1.2	1.99	9.0×10^{-3}
	2.2	2.14	9.0×10^{-3}
WO$_3$ Schuchardt	0.9	1.77	9.0×10^{-3}
	2.2	1.84	9.0×10^{-3}
	1.3	1.95	6.0×10^{-3}
	2.2	2.12	9.0×10^{-3}
WO$_3$ neutron diffraction	1	1.74	
	2	1.84	
	1	1.92	
	2	2.11	

4. Results and discussion

The FT for the ammonium metatungstate sample before (Fig. 5*a*) and after testing the cell for the *in situ* decomposition (at 773 K in flowing dry oxygen) to tungsten trioxide (Fig. 5*b*) confirmed that the cell operated properly. The ammonium metatungstate sample had a double peak in the 0.80–2.30 Å range and a peak in the 2.30–3.90 Å range. Crystallographic data for the compound show that W atoms are in a distorted octahedral coordination with W—O bond lengths ranging from 1.70 Å to 2.20 Å, and described as having, on average, four W—O bond lengths equal to 1.92 Å, a longer one equal to 2.26 Å and a shorter bond length equal to 1.70 Å, due to a terminal W—O bond. On this basis a curve-fitting of the first coordination shell, in the range 0.80–2.30 Å, was performed (Fig. 6). In order to obtain the best agreement between experimental and calculated spectra, a set of three different W—O bond lengths was used, as suggested by crystallographic data.
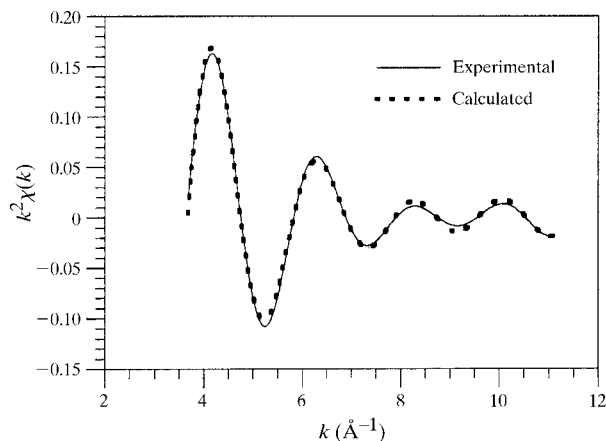
Results are reported in Table 1. The second peak in the FT is due to W—W distances ranging from 3.65 Å (W—O—W bonds) to 3.30 Å ($W<^O_O>W$ bonds) (Fuchs & Flindt, 1979).

The FT for ammonium metatungstate after *in situ* thermal treatment (Fig. 5*b*) showed the first coordination shell peaks in the 0.80–2.20 Å interval, a multiple scattering peak (MS) in the 2.20–3.20 Å range and the second coordination shell peak in the 3.20–4.50 Å range. The comparison between the FT of the *in situ* treated sample (Fig. 5*b*) and that of commercial WO$_3$ (Schuchardt) (Fig. 5*c*) revealed that ammonium metatungstate underwent thermal decomposition to WO$_3$. In order to investigate some possible differences between these compounds, curve-fitting of the first coordination shell, in the range 0.80–2.20 Å, was performed in both cases (Figs. 7 and 8). Best fits were obtained by introducing four different W—O distances as suggested by Balerna *et al.* (1991). Results (see Table 1) showed that the first-shell W—O distances for the *in situ* treated sample are a little longer than those for the commercial compound. Our fitted distances are in good
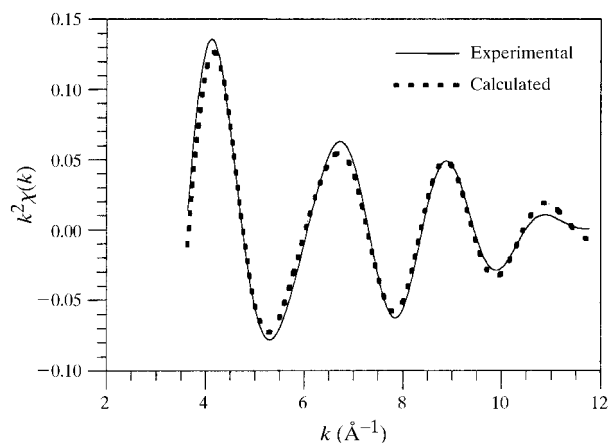

Figure 7
In situ treated sample: experimental and calculated curves $k^2\chi(k)$ for the first coordination shell (R = 0.80–2.20 Å).
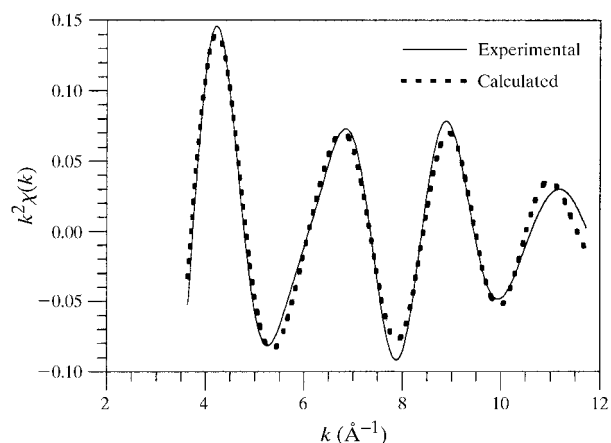

Figure 6
Ammonium metatungstate: experimental and calculated curves $k^2\chi(k)$ for the first coordination shell (R = 0.80–2.30 Å).

Figure 8
WO$_3$ (Schuchardt): experimental and calculated curves $k^2\chi(k)$ for the first coordination shell (R = 0.80–2.20 Å).

agreement with the data reported by Loopstra & Boldrini (1966) for monoclinic WO_3 and obtained by powder neutron diffraction. In order to compare our fitted $W-O$ bond distances by EXAFS spectroscopy with those by neutron diffraction we made an average on the two sets of bond lengths reported by Loopstra & Boldrini (1966) for the two different W sites. It resulted that monoclinic WO_3 can be described as WO_6 octahedra having one short $W-O$ bond length equal to 1.74 Å, two $W-O$ lengths equal to 1.84 Å, one equal to 1.92 Å and two long $W-O$ bond lengths equal to 2.11 Å. The agreement with our data is very good (Table 1).

5. Conclusions

We have designed and assembled a simple and not too expensive cell for *in situ* investigations, at both high and low temperature, in transmission and fluorescence XAS spectroscopy. After some preliminary tests we verified that the cell worked properly to obtain the *in situ* decomposition of an ammonium metatungstate sample, the EXAFS spectrum of which was analysed. After *in situ* heating at 773 K, 1 h in a dry oxygen flow, ammonium metatungstate was transformed into monoclinic WO_3.

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