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XAFCA: a new XAFS beamline for catalysis research

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A new X-ray absorption fine-structure (XAFS) spectroscopy beamline for fundamental and applied catalysis research, called XAFCA, has been built by the Institute of Chemical and Engineering Sciences, and the Singapore Synchrotron Light Source. XAFCA covers the photon energy range from 1.2 to 12.8 keV, making use of two sets of monochromator crystals, an Si (111) crystal for the range from 2.1 to 12.8 keV and a $KTiOPO_4$ crystal [KTP (011)] for the range between 1.2 and 2.8 keV. Experiments can be carried out in the temperature range from 4.2 to 1000 K and pressures up to 30 bar for catalysis research. A safety system has been incorporated, allowing the use of flammable and toxic gases such as H_2 and CO.

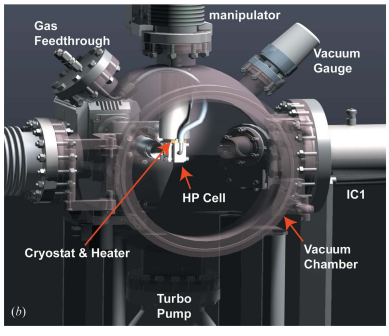
1. Introduction

XAFCA is an XAFS (Sayers *et al.*, 1971) beamline for heterogeneous catalyst research, funded by the Science and Engineering Research Council (SERC) of the Agency for Science, Technology and Research (A*STAR), Singapore. The beamline was officially opened to users in late 2011. It is located at the Singapore Synchrotron Light Source (SSLS) (Moser *et al.*, 2004) at the National University of Singapore (NUS). The beamline is based on a compact 700 MeV electron storage ring that produces synchrotron radiation from two 4.5 T superconducting dipoles. The critical energy is 1.47 keV and currents in excess of 300 mA with a lifetime of 12 h are routinely produced.

2. Beamline overview

2.1. Beamline

The beamline layout, shown in Fig. 1, is similar to a standard XAFS beamline, consisting of a front end, a collimating mirror (CM), a double-crystal monochromator (DCM), a focusing mirror (FM) and an endstation. To cover the full energy range from 1.2 to 12.8 keV, two sets of crystals are employed in the DCM chamber, which are Si (111) for the range between 2.1 and 12.8 keV and a $KTiOPO_4$ crystal [KTP (011)] for the low-energy range from 1.2 to 2.8 keV. The second crystal of Si (111) is a sagittally bent crystal (Freund *et al.*, 1998) with a variable curvature radius (R_{min} = 1 m). The maximum horizontal acceptance angle is 8 mrad. The DCM has a fixed exit with an offset upwards of 35 mm. The maximum speed of the Bragg rotation is $1^\circ\ s^{-1}$, which makes it suitable for quick-XAFS. To optimize reflection and focusing, there are two stripe-like areas with different coating materials for each mirror, *i.e.* carbon for 1.2–2.8 keV and Rh for 2.1–12.8 keV. In the case of the focusing mirror, two different types of curved



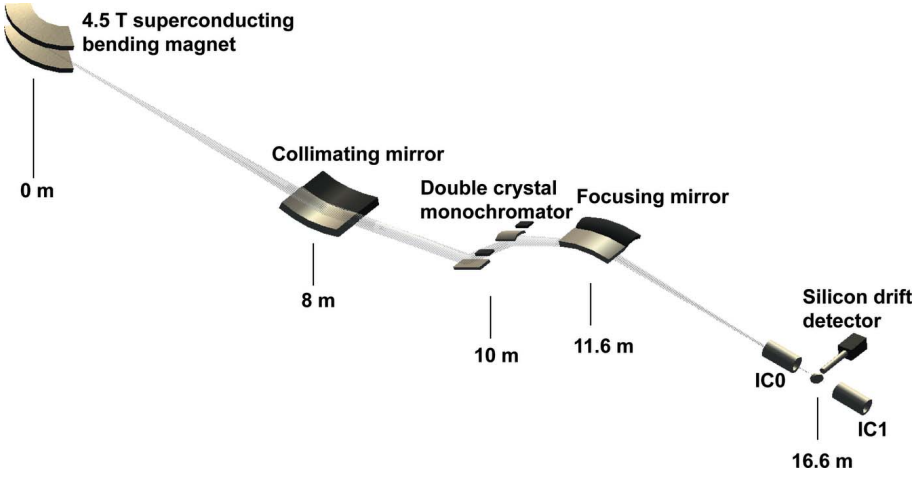


Figure 1
Schematic view of the XAFCA beamline. The collimating mirror makes the beam vertically parallel, upstream of the double-crystal monochromator (DCM), and the focusing mirror refocuses the beam at the sample position. There are two sets of crystals in the DCM, Si (111) and KTP (011). The second Si (111) crystal provides sagittal (horizontal) focusing, which is also applied in the beamline I811 at MAX-lab (Carlson *et al.*, 2006).

Table 1
The XAFCA beamline specifications.

Source type:	4.5 T superconducting bending magnet
Mirror 1	Stripe 1: vertical collimating mirror with Rh coating Stripe 2: vertical collimating mirror with C coating
DCM	Set 1: Si (111) with second sagittally bent crystal Set 2: KTP (011)
Mirror 2	Stripe 1: vertical focusing mirror with Rh coating Stripe 2: toroidal mirror with C coating
Energy range	1.2–12.8 keV
Resolution	5.1×10^{-4} at 10 keV
Temperature at sample	4.2–1000 K
Pressure at sample	10^{-6} mbar–1 bar, 1 bar–30 bar
Gases available	H_2, CO, O_2, air, N_2, Ar and He (others: upon request)
Beam size	Typically 1.5 mm (H) × 0.5 mm (V)
Flux at sample	1.6×10^{10} photons s^{-1} at 7 keV, 300 mA (measured)

surface were chosen, namely, the stripe for 2.1–12.8 keV is cylindrical for vertical focusing and the stripe for 1.2–2.8 keV is toroidal. The CM and the first crystal of the DCM are water-cooled. The flux at the sample position is about 1.6×10^{10} photons s^{-1} at 7 keV for a stored beam current of 300 mA (measured using a calibrated photodiode). The main parameters of the XAFCA beamline are summarized in Table 1.

2.2. Endstation

The XAFCA endstation was designed for easy switching between low-energy and hard X-ray modes. Low-energy X-ray mode is used for photon energies below 3 keV, while a hard X-ray mode uses photon energies above 2.4 keV. During low-energy X-ray operation, the valves V7, V9, V10 are open and V8 is closed, see Fig. 2. A 300 nm-thick Ni foil detector (ND) is used to measure the beam intensity. V8 is a 15 µm-thick polyimide window installed on a pneumatic gate valve to prevent the optical components from being polluted by the samples. The pressure in the vacuum chamber is normally better than 10^{-4} mbar. During hard X-ray operation, V8 is open while the rest of the valves remain closed, the opposite of low-energy X-ray operation. The ionization chamber, IC0, is used to measure the beam intensity. The beryllium windows of IC0 are installed on two pneumatic gate valves, V9 and V10. All gate valves in the XAFCA endstation are monitored and controlled by the equipment protection system (EPS). The programmable logic controller of EPS blocks any incorrect operation, such as opening V7 when the pressure in the vacuum chamber is still poor, to protect the upstream vacuum. The vacuum chamber, shown in Fig. 2, is where the samples are loaded for analysis. A manipulator which is equipped with a cryostat and an oven is mounted on the top of the chamber to transfer and rotate samples along the z direction. The cryostat and oven can provide a temperature range from 4.2 to 1000 K. A 270 l s^{-1} turbo pump is connected at the base of the vacuum chamber and it is able to pump the chamber from atmospheric pressure to 10^{-4} mbar vacuum in a few minutes (the best vacuum can reach 10^{-6} mbar).

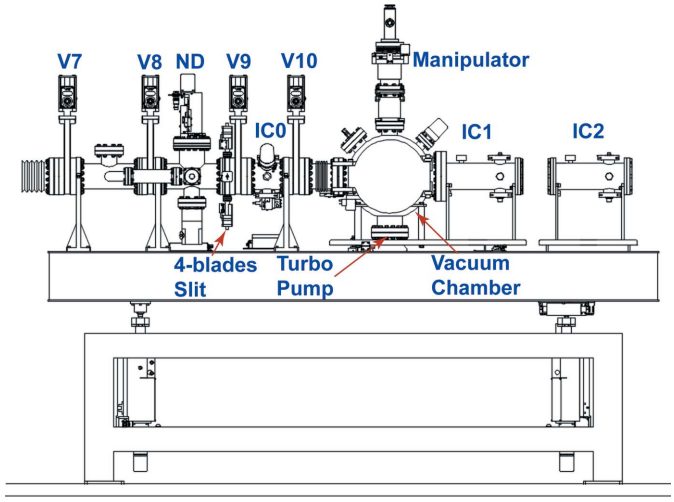


Figure 2
Side view of the XAFCA endstation. V7 is a 150 µm beryllium window installed on a pneumatic gate valve to isolate the vacuum of the storage ring, front end and optical components from the endstation. V8 is a 15 µm polyimide window installed on a pneumatic gate valve to prevent the optical components from being polluted by the samples. ND is a 300 nm Ni foil detector to monitor the intensity of the X-rays with an energy below 3 keV. IC0 is an ion chamber to monitor the intensity of incident X-rays with an energy above 2.4 keV. The vacuum chamber is where samples are placed. A 270 l s^{-1} turbo pump is connected at the bottom of the vacuum chamber. A manipulator equipped with a cryostat and oven system is mounted on the top of the chamber to transfer and rotate samples along the z direction (vertical direction). The cryostat and oven system can provide a temperature range from 4.2 to 1000 K.

Both transmission and fluorescence modes are available at XAFCA for XAFS data collection. For transmission mode, one custom-designed ionization chamber and two IC-Spec ionization chambers (FMB-Oxford) are used. A gas system with He, N_2 and Ar is connected to the ion chambers to change gas type and pressure to optimize the current in the ion chambers. The pressure of IC0 and IC1 can be adjusted from 1 mbar to 1.5 bar. The fluorescence yields from the sample can be measured using a silicon drift detector (Bruker XFlash 6|100), which has a 100 mm^2 active area in a single element and a 600 Kcounts per second pulse loading capability.

2.2.1. *In situ* cells. For *in situ* XAFS experiments, a series of sample cells have been developed. Sample cells are available for temperatures from 4.2 to 1000 K operating under vacuum or atmospheric pressure and for temperatures from 200 K to 770 K and pressures up to 30 bar. Fig. 3(*a*) shows a schematic drawing of the high-pressure cell. The main body is made of stainless steel and the windows are made of beryllium. The reaction cell is sealed using silver gaskets. Fig. 3(*b*) shows how the high-pressure cell is mounted on the cryostat and heater. The maximum temperature and pressure for this cell are 700 K and 30 bar, respectively. H_2, CO, O_2, air, helium and other gases are available at XAFCA.

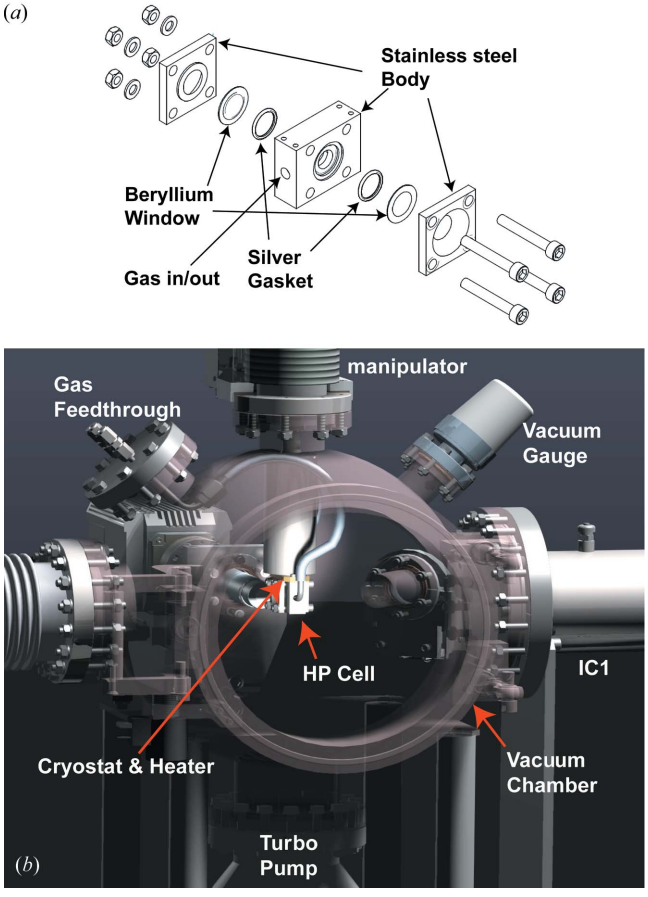


Figure 3
(*a*) Schematic drawing of the high-pressure cell. (*b*) View of the vacuum chamber showing how the cell is mounted on the cryostat and heater inside the vacuum chamber.

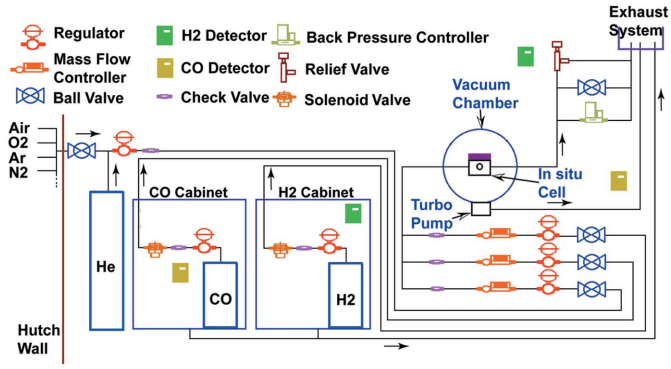


Figure 4
Schematic drawing of the high-pressure gas supply system. Gas detectors for CO and H_2 are installed in both cabinets and the experimental hutch. The installation height for the CO detector in the hatch is roughly 1.5 m. The H_2 detector in the hutch is installed on the ceiling. If a leakage is detected, the control panel will shut down the solenoid valves automatically and increase the speed of the fan to full speed which, under normal operation, runs at half of its maximum speed.

2.2.2. High-pressure gas supply system. To supply high-pressure gas to the *in situ* cell, a high-pressure gas supply system was built. A schematic drawing of the system is shown in Fig. 4. Three different gases can be mixed for an *in situ* study. The maximum flow is 100 ml min^{-1} for each channel. A back pressure controller is used to adjust the pressure from 0 to 30 bar. The gas cabinets, vacuum chamber and the outlets of the pipelines are connected to the exhaust system. Gas detectors for CO and H_2 are installed in both cabinets and the experimental hutch. If a leak is detected, the control system will shut down the solenoid valves automatically and increase the speed of the exhaust fan to full speed, which normally runs at half speed. The whole system has been tested by the Singapore Civil Defence Force (SCDF) and XAFCA obtained the certificate from SCDF to use H_2 and CO on 27 February 2013.

2.3. DAQ system

The XAFCA data acquisition (DAQ) system was developed using Labview. The system was stable during 2000+ hours of testing. The XAFCA DAQ system provides functions of conventional scan, quick scan, multiple scan, automatic scan, real-time data comparison and detectors setup as well. A quick scan usually takes around 90 s for a full-range scan: from −150 eV below the edge to 800 eV above the edge. The automatic scan function allows up to a maximum of five samples to be measured automatically. The data file format of the XAFCA DAQ sytem is an ASCII file, which is compatible with most common XAFS data analysis software such as *IFEFFIT* and *WinXAS*.

3. Facility access

The XAFCA beamline is operated by the Institute of Chemical and Engineering Sciences, A*STAR. The beamline is open to users from universities, industry, government

agencies and research institutes worldwide for scientific investigations in the area of catalysis and materials science. Prospective users are encouraged to contact the XAFCA staff members for more details on the capabilities of the XAFCA beamline. Online booking is available at the user portal of SSLS (http://ssls.nus.edu.sg).

4. Testing and preliminary results

To test the XAFCA beamline, XAFS data of a standard Cu foil and $CuSO_4$ (S *K*-edge) were collected. Fig. 5 shows the XANES of Cu along with the k^3-weighted EXAFS data in *k* space. The energy resolution of XAFCA at the Cu edge is about 4 eV, which is insufficient to resolve the shoulder peak. Fig. 6 shows the S *K*-edge XANES of $CuSO_4$ obtained in fluorescence mode at XAFCA. Fig. 7 shows the Fe *K*-edge XANES of an Rh–Fe/Ca–Al_2O_3 catalyst (Choong *et al.*, 2014) reduced in flowing H_2. As reported in this reference, an XAS study was performed to unravel the presence of Fe_xO_y species upon reduction, which is crucial for CO-free hydrogen production using low-temperature ethanol steam reforming.

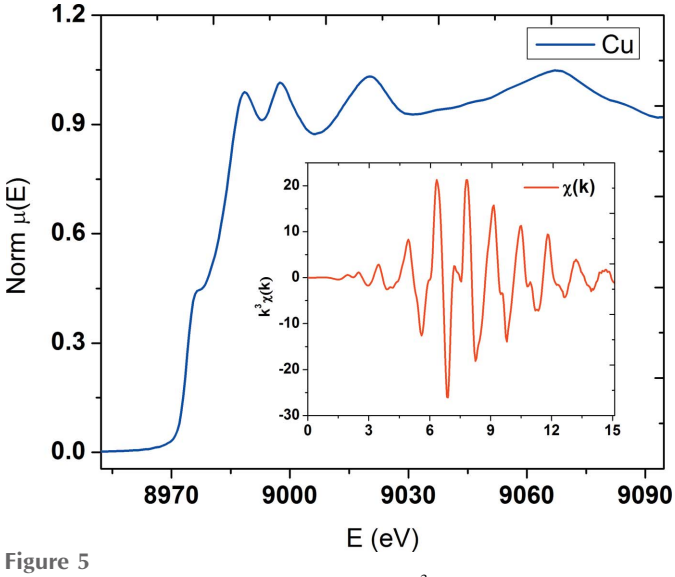


Figure 5
XANES data of Cu *K*-edge along with the k^3-weighted EXAFS data.

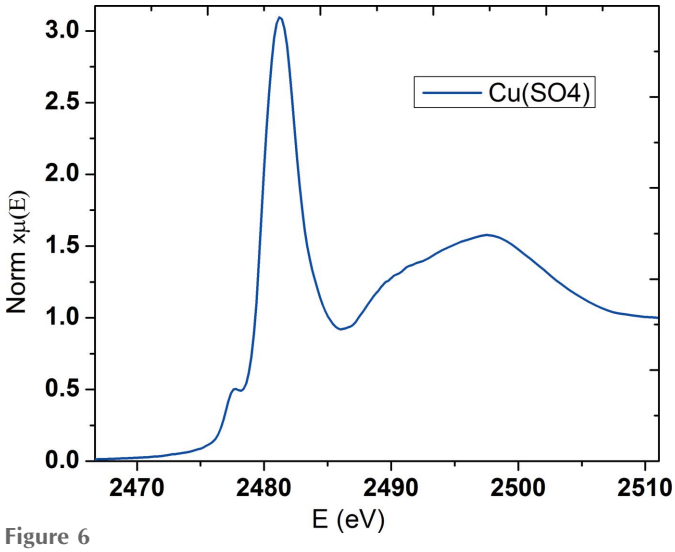


Figure 6
S *K*-edge XANES of $CuSO_4$.

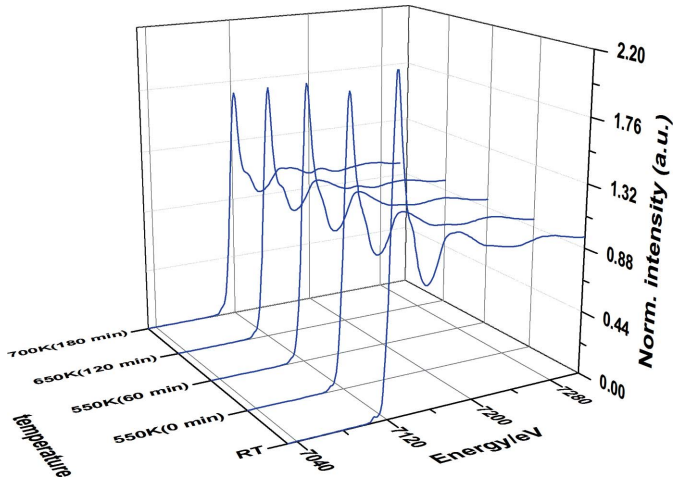


Figure 7
Fe *K*-edge XANES of an Rh–Fe/Ca–Al_2O_3 catalyst reduced under flowing H_2. The catalyst was reduced in 10% H_2 mixed with He at three different temperatures, 550, 650 and 700 K, with a heating rate of 10 K min^{-1}. The temperature was held for one hour at each temperature mentioned above. Five XANES spectra were selected from hundreds of data sets to follow the reducibility of this catalyst.

Recently, a study using XAFS unravelling the existence of short Pt–Pt interactions in a MOF-253-Pt photocatalyst was published (Zhou *et al.*, 2013). MOF-253-Pt is a bifunctional photocatalyst for hydrogen evolution under visible-light irradiation. These Pt–Pt interactions, which are believed to play a key role on the photocatalytic activity, can be hardly detected using other methods. Another EXAFS study performed at XAFCA on bimetallic catalysts shows the existence of an Ni–Cu alloy in an Ni–Cu/CeO_2 bimetallic catalyst (Saw *et al.*, 2014). This catalyst was designed for high-temperature water–gas shift reaction. The catalytic results show that the catalyst exhibits the highest reaction rate and the lowest methane selectivity when the Ni/Cu ratio is equal to 1. This behaviour results from the formation of an Ni–Cu alloy phase, which was unravelled by XAS experiments.

5. Discussion and conclusion

The XAFCA beamline is optimized for catalysis research using XAFS. The flux and beam size allow for the acquisition of high-quality XAFS data. Transmission and fluorescence modes are currently available, while total electron yield mode will be available next year. The endstation can provide temperatures from 4.2 to 1000 K and a pressure up to 30 bar for *in situ* XAFS studies. H_2 and CO can be used for *in situ* experiments with high safety standards. To further enhance the capabilities for *in situ* studies, reaction cells for liquids are under design. A mass spectrometer will be installed to analyse the reaction products. In future, an image plate will be

installed to perform combined XAFS and X-ray diffraction *in situ* studies.

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