# Chapter 6
# Cell Designs for In Situ and *Operando* Studies

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## 6.1 Introduction and Criteria for the Choice of an Appropriate Cell

The design of appropriate spectroscopic cells for in situ and *operando* XAFS studies of heterogeneous catalysts has been a very active field during the past decades as the investigation of catalysts at work has become a powerful approach to improve the activity and selectivity of catalysts in a rational manner [1–4]. The inherent advantage of X-rays is due to their penetrating power through solids, gases and liquids. The structural information can be gained under reaction conditions with reactors with similar geometry to those used in industrial catalysis. Various cells for in situ (e.g., in a gas atmosphere) or *operando* (i.e., while measuring the catalytic performance) spectroscopic studies have already been designed since the 1980s [5].

Still, during the past years a number of new in situ cells have been developed, e.g., to combine XAFS with complementary techniques [6], to optimize the geometry for XAS in fluorescence mode [7], to investigate heterogeneous catalysts in liquid phase [8] or to extend in situ XAS studies to high pressure reactions [9]. Hence, many different cell designs exist, which are mostly unique and tailored to a specific application. Only a few of them are commercially available [9, 10], and most of them are constructed by the research groups themselves. Recently, attempts to exchange experience and develop infrastructure for catalysis studies at synchrotrons emerged for example in the US (Synchrotron Catalysis Consortium, SCC) [11] as well as in Europe (e.g., SNBL [12, 13] and DUBBLE [14] beamlines at ESRF, SAMBA beamline [9] at SOLEIL and catalysis research at ANKA [15]).

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Many of these organizations even provide infrastructure and support for the users without synchrotron experience; however, choosing an appropriate cell is a critical decision for a successful experiment.

The reasons for the wide variety of in situ cells are manifold. One of the main reasons is the high number of different applications. A spectroscopic cell for studying a catalyst while it is working (e.g., in a fast reaction) needs a completely different design than a cell for a catalyst that acts in a slow reaction which is not mass transfer limited, a reaction in liquid phase or an experiment where the catalyst is studied after reduction. Grunwaldt et al. [16] have described criteria to guide this development of in situ cells from the start of the construction to aim finally at the "best compromise"; many of those criteria are similar to those in the chemical engineering literature. An overview on different spectroscopic cells and the history of development of the in situ cells for XAFS studies of catalysts was furthermore given by Bare and Ressler [17]. The following considerations are important when choosing the appropriate cell:

- Are the data to be collected in transmission or in fluorescence mode? This depends on a number of factors including the nature of the sample (concentration of the element of interest and homogeneity of its distribution in the sample), the experimental design, and the necessity to combine XAFS with other spectroscopic techniques.
- The range of the photon energies to be covered. This is crucial for choosing the appropriate material and the thickness of X-ray windows.
- Operating temperatures and pressures as well as chemical compatibility of reactants with window, reactor and sealing materials. Maximum heating and cooling ramps, which are limited by the thermal mass of the cell.
- In case of catalytic reactions: Is the reaction fast or slow (internal mass transport limitations)? Does it occur in gas phase or liquid or even three-phase mixture (external mass transport limitations)?
- Are accurate measurements of catalyst activity, selectivity, and the temperature of the catalyst bed necessary? In particular, will the measurements be carried out under *operando* conditions?
- Are specific safety issues to be considered?
- Are spatially or time resolved studies (resolution) required?
- Should the XAS experiment be combined with other spectroscopic techniques?

Irrespective of the type of the cell an important decision has to be made concerning the X-ray transparent window material. The material has to absorb the minimum amount of incoming, transmitted and/or fluorescence X-rays and needs to be chemically, temperature, and mechanically stable for the desired application. The most commonly used X-ray window materials include beryllium, Kapton® (polyimide), quartz, glassy carbon, and boron nitride. For high pressure in situ cells and studies at higher photon energies (typically more than 10 keV) foils of light metals, e.g., Al or Ti can serve as X-ray windows. If a combination of techniques is required the window has to be transparent for all used photon energies, e.g., when combining XAS with simultaneous Raman measurements quartz reactors [13] or cells with mica windows [9] are used.

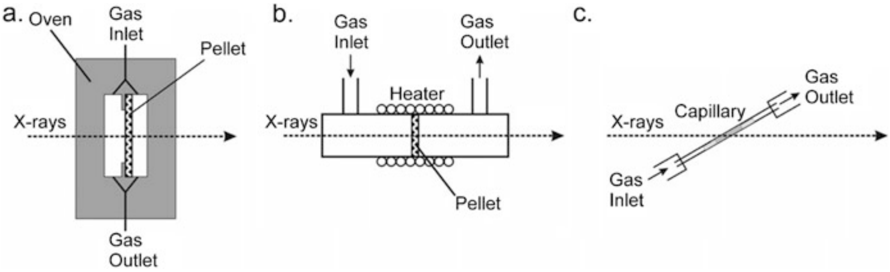


**Fig. 6.1** Typical designs of in situ cells for studies of heterogeneous catalysts: (**a**) environmental cell with gas flowing around a pellet and (**b**) a cell with gas flowing through a pellet; (**c**) capillary microreactor cell with plug-flow reactor geometry for studying powder catalysts. Reproduced from ref. [16] with permission from the PCCP Owner Societies

In general, a cell design fulfilling all wishes of an experimentalist is rarely possible or available which results in compromises between the XAFS data quality and catalytic performance, easiness of operation, safety, and many more aspects. A comparison of in situ cells of principally different design concepts in terms of both spectral data quality and the relevance for the reaction kinetic (*operando*) measurements was reported by Grunwaldt et al. (Fig. 6.1) [16]. The more common design with a catalyst wafer (pressed pellet) placed in an environmental cell with gas flowing around the pellet (Fig. 6.1a) showed its suitability for obtaining good spectral quality data with homogeneous beam transmission. This makes this cell type suitable also for measurements with position-sensitive detectors, i.e., for energy dispersive EXAFS. An improved design of this cell, which is also used for infrared spectroscopy [18], involves gas flowing through a pellet (Fig. 6.1b). This design ensures gas diffusion through the entire cross section of a sample pellet; however, it requires preparation of pellets with sufficient porosity, e.g., using γ-alumina as a binder material which is not always possible without altering the catalytic properties of the sample material [16]. The other cell in the comparison was a capillary microreactor as example of plug-flow reactor geometry and catalyst in form of 80–120 μm particles (Fig. 6.1c), based on concepts by Clausen et al. [19] and Thomas et al. [20], and a powder sample in an enclosed cell reported by Bazin et al. [21]. While the pellet cell allowed higher quality XAFS data acquisition, the diffusion limitations through a catalyst wafer resulted in markedly different kinetics during temperature-programmed reduction of CuO/ZnO when compared to catalyst grains such as in a capillary cell. In the case of fast catalytic reactions (e.g., oxidation of methane over $PdO_x/ZrO_2$) gas bypass in the pellet cell and especially internal mass transport limitations were shown not only to significantly influence the measured catalytic data but also falsify conclusions on the structure since only the outer surface is really exposed to the reaction mixture [16].

The reason for different kinetics of Cu reduction is just due to internal mass transfer limitations as demonstrated in ref. [16]. For spherical particles the reaction time $\tau$ can be calculated using the shrinking core model:

$$\tau_{\mathrm{internal}} \cong \frac{\rho_{\mathrm{CuO}} \cdot R_{\mathrm{p}}^{2}}{3D_{\mathrm{e}} \cdot c_{\mathrm{H2}}} \tag{6.1}$$

where $\rho_{\mathrm{CuO}}$ is the molar density of CuO in a particle, $D_{\mathrm{e}}$ is the effective diffusion coefficient, $R_{\mathrm{p}}$ is a particle radius (or pellet thickness), and $C_{\mathrm{H2}}$ is the hydrogen concentration. For an effective diffusion coefficient of $10^{-6}$–$10^{-8}$ m$^2$/s and a 100 μm particle $\tau$ amounts to 20 ms–2 s. This is already in the time range of time resolved studies using QEXAFS [22] and DEXAFS [23] and should be taken into account, i.e., a reaction faster than ≈1 ms may be hampered by internal diffusion or external mass transport, even in the ideal case of a sieved catalyst. Similar considerations apply to pressed catalyst wafers (pellets) where the total reduction time with the diffusion coefficients given above and 2 mm pellet thickness amounts to 33 s–56 min (depending on the porosity of the binder material) which makes it inapplicable for time-resolved experiments.

Internal mass transport may not only play a role during dynamic changes of temperature or concentration but also may even occur under stationary reaction conditions if the reaction rates are high such as for oxidation of methane. In heterogeneous catalysis, this is typically reflected by the "effectiveness factor" of the catalyst and estimated using the Thiele modulus [24]. Due to the high reaction rate the reactant (e.g., methane) is already consumed while diffusing into the porous solid catalyst and the inner part of the catalyst may thus not interact with the reactant at all. Since XAS experiments typically probe the whole catalyst and average the contributions from all atoms of a specific element, this will also strongly affect or even falsify the spectroscopic result.

Figure 6.2 shows an example of a methane concentration gradient calculated for the total oxidation of methane over Pd-based catalysts based on a reaction rate constant $k_{\mathrm{r}} = 1.55 \cdot 10^{3}$ s$^{-1}$ and an effective diffusion coefficient $D_{\mathrm{e}} = 1.1 \cdot 10^{-6}$ m$^2$ s$^{-1}$ [16]. Whereas the concentration in an 80 μm large particle (sieved catalyst) only drops to 90 % of the surface concentration, the concentration of methane in a self-supporting disk drops to less than 10 % already at a penetration depth of 70 μm. This means that, in case of a net wafer thickness of 1 mm, transmission XAS will only to

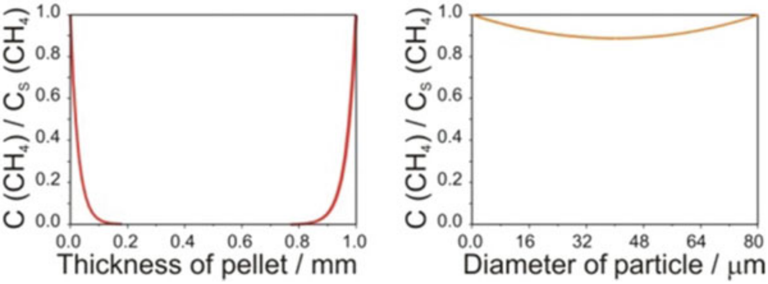


**Fig. 6.2** Calculated profiles of the methane concentration (normalized by the surface concentration) during the total oxidation of methane for the cases of a 1 mm thick pellet and an 80 μm particle. Adapted from ref. [16] and ref. [25] with permission from the PCCP Owner Societies

a *minor* extent monitor the area within the catalyst where the reaction occurs. The effectiveness for a pressed wafer is with 3 % much lower than for a particle of 80 μm (88 %). For a Thiele modulus

$$\psi = L_c \sqrt{\frac{k_r}{D_e}} \leq 3 \tag{6.2}$$

the methane concentration drops to less than 10 % at the center of the catalyst particle ($L_c$ is a characteristic length defined as half of the thickness for a disk and 1/6 of the particle diameter for round-shaped particles, cf. ref. [24]; $k_r$ is the rate constant). Hence, the Thiele modulus is a very useful parameter which indicates whether internal mass transport is limiting and thus well suited for optimizing in situ and, especially, *operando* spectroscopic cells.

In conclusion, for fast reactions a finely sieved powder catalyst should preferentially be used. Similar considerations as for gas phase experiments can be made for liquids and higher pressure studies, where also external mass transport limitations at the fluid/solid interface may occur [16]. This compromise keeps the design of new in situ cells a very active field to fulfill the best spectroscopic conditions (depending on the photon energy, concentration of the element of interest as well as the required spatial resolution) and optimum catalytic conditions (gas phase, liquid phase, high pressure, temperature profiles, mass transfer limitations, continuous flow or batch-like). Therefore, there cannot be a universal solution. Instead, different applications require specific cell designs.

## 6.2 In Situ Cells for Studies of Catalysts in Form of Powders and Pellets

One of the first cells for the in situ XAFS studies of catalysts was designed by F. Lytle et al. [5]. The design (Fig. 6.3) has been adopted by many research groups and it is one of the few commercially available cells [26]. It allows transmission measurements on both self-supporting wafers and powders using a special boat-type inset. An additional ion chamber detector with a built-in amplifier is available for measurements in fluorescence mode. The gas atmosphere may be changed and the cell can be evacuated. The maximum pressure is rated up to 100 bar. It is possible to cool the sample holder with liquid nitrogen and to heat it up to approx. 1000 K using a built-in resistance heating unit. At the same time the outer shell of the cell is water-cooled to prevent heating the beamline components and the fluorescence detector. One downside of the design is the gas bypassing the sample which prevents obtaining quantitative catalytic data acquisition. The other drawback is that the temperature of the catalyst sample cannot be measured directly.

A significant improvement of the same general layout was reported by Hannemann et al. (Fig. 6.4) [7]. This cell allows measurements on (preferentially)

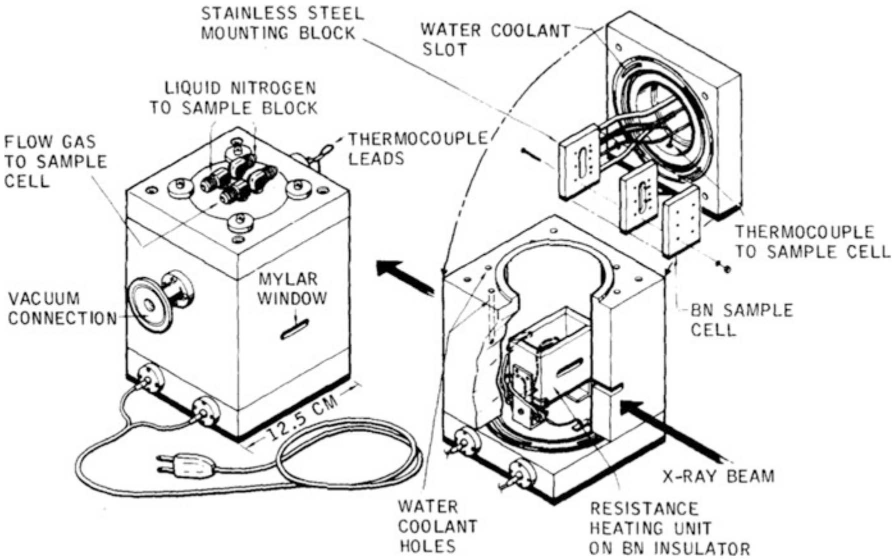


**Fig. 6.3** Schematic view of the Lytle cell. Reprinted with permission from ref. [5]. Copyright 1979, AIP Publishing LLC

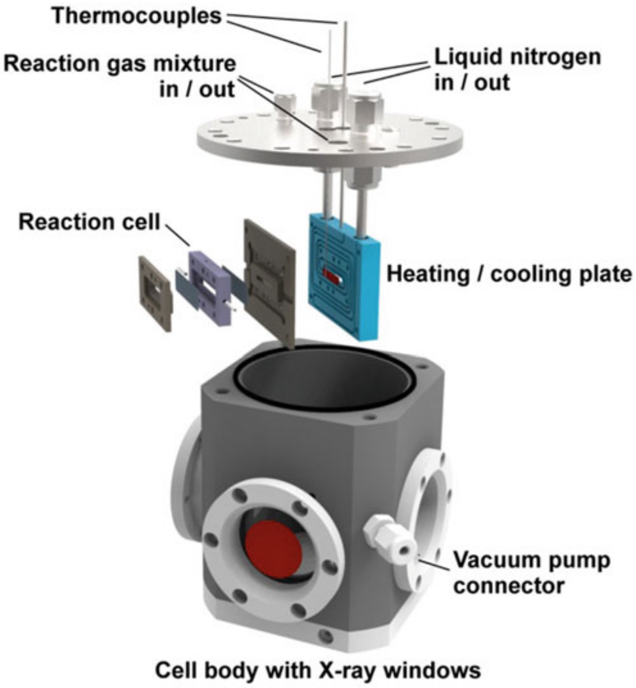


**Fig. 6.4** Schematic view of the XAFS cell for transmission/fluorescence measurements and X-ray diffraction

powders (like the cell by Bazin et al. [21]) and self-supported wafers (pressed into the sample compartment). It mimics a plug flow reactor, is suitable for both gas and liquid environments and additionally allows online products analysis. The sample holder further allows cooling down to the temperature of liquid nitrogen and heating to 973 K. The heating is localized so that the temperature of the outer body does not exceed 423 K even without water cooling. The inner volume of the cell can be evacuated (e.g., to prevent ice formation on the X-ray windows during measurements at liquid nitrogen temperature) or filled with He for measurements at low energies. Different materials can be used for the sample holder depending on photon energy, pressure and the chemical nature of reactants/products. The thickness of the sample can be varied by using reaction cell insets of different thickness. A variable sample positioning angle relative to the beam, wide windows and funnel-shaped cutouts in the sample holder allow measurements of X-ray fluorescence and X-ray diffraction simultaneously with XAFS measurements in transmission mode. Notably, due to the windows on all four sides of the cell it can be used at many different beamlines with different detector arrangement.

A much simpler but not less versatile cell was originally suggested by Clausen et al. [19] and Thomas et al. [20], and further developed by Grunwaldt et al. (Fig. 6.5a) [16]. The concept is based on a thin quartz (or glass) capillary (0.5–3 mm o.d., 10–20 μm wall thickness, available from for example Hilgenberg GmbH, Hampton Research, and a number of other suppliers) connected to a gas dosing and a gas analysis units by means of graphite ferrules [16] or high-temperature epoxy glue for gas-tight sealing [27]. The catalyst, in form of small grains (grain size is typically within 50–150 μm range), is placed between two quartz wool plugs, and the overall assembly has a geometry of a regular plug-flow catalytic reactor with virtually no dead volume. The capillary can be cooled or heated by cold or hot nitrogen (air) blowers. Some of them are commercially available, e.g., a Cryojet from Oxford Instruments (85–500 K) [28] and a gas blower built by Cyberstar S.A. (now by FMB-Oxford, heating up to 1273 K) [29]. An alternative air blower LE Mini Sensor

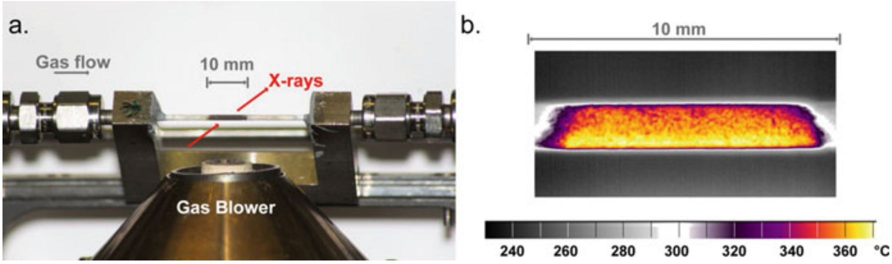


**Fig. 6.5** (**a**) A photograph of the capillary cell used by Grunwaldt et al. [16], here mounted on top of a FMB Oxford Gas Blower (heater). The capillary microreactor is glued in the stainless steel holder by means of high-temperature epoxy-glue. (**b**) IR thermography image of the temperature distribution in a microreactor capillary filled with a Pt/$Al_2O_3$ catalyst at 400 °C Gas Blower setpoint in a flow of 50 ml/min He

from Leister Technologies AG originally designed for the plastic packaging industry can be used up to 900 K [26].

The remarkable versatility of this design allows simultaneous measurements of X-ray absorption, fluorescence, diffraction [6], and also optical spectroscopy such as Raman [6, 13] or UV–Vis [30]. The capillary microreactor cell is also suitable for studies of photocatalysts under working conditions [31]. Catalytic data can be measured and evaluated as for any conventional plug-flow reactor. There are certain drawbacks of the design, which should be taken into account when planning an experiment. First of all, precise measurement of the catalyst temperature is not possible, second, as for all plug-flow reactors, in case of fast reactions concentration gradients along the catalyst bed will occur [32]. Furthermore, although the cell was tested under pressures up to 50 bar [19], the actual maximum pressure depends on the particular capillary and cannot be defined a priori. Heating by a gas stream leads to temperature gradients (e.g., Fig. 6.5b) which may be critical and should be taken into account for certain catalytic reactions, e.g., total oxidation [33] with steep light-off curves. Some of the drawbacks can be negotiated with, i.e., heating of the catalyst by the intense X-ray beam can be estimated based on the change in the catalytic conversion [34], and in the case of concentration gradients spatially resolved XAS measurements are required [32, 35].

For high throughput X-ray absorption studies (to increase the number of measured catalysts) also a microreactor array was developed that allows to study the structural changes in six to ten solid samples with an independent gas supply to each reactor channel and also fast independent MS analysis [36, 37] and thereby real simultaneous *operando* acquisition of XANES spectra of working catalysts. The setup uses a fast CCD camera with X-ray absorption contrast as is schematically shown in Fig. 6.6.

Application of thin walled quartz capillaries limits the maximum pressure and requires several safety precautions against breaking the capillary. Other materials

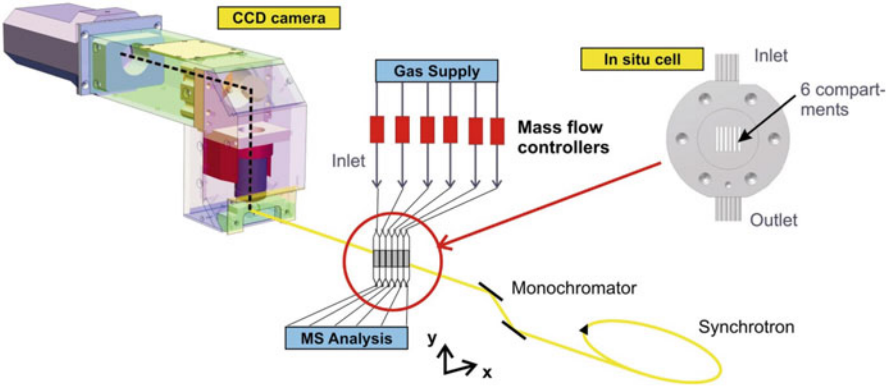


**Fig. 6.6** Setup for parallel screening of the structure of heterogeneous catalysts at work using a CCD camera and a microreactor array. Reproduced from ref. [37] with permission.© IOP Publishing. All rights reserved

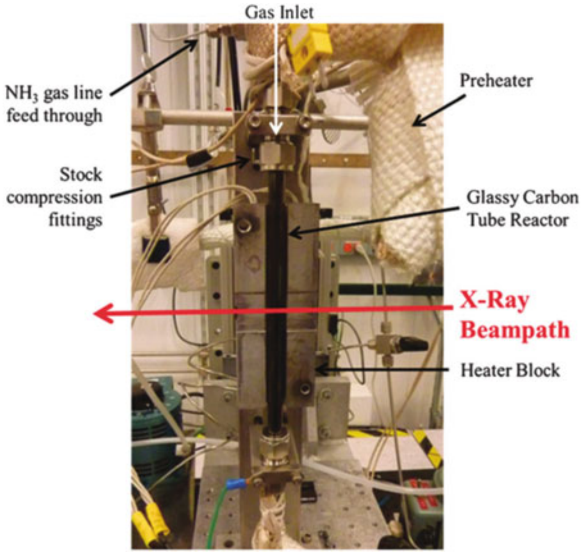
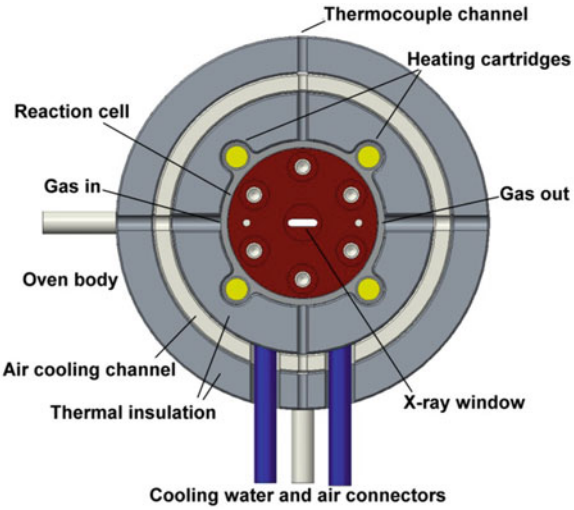


**Fig. 6.7** A glassy carbon reactor installed in a heater block as reported by Kispersky et al. [40]. Reproduced from ref. [40] with permission of The Royal Society of Chemistry

with lower X-ray absorption than that of quartz were suggested for use as plug-flow microreactors. Bazin used carbon foil [21], Bare used Be tubes with 3 mm outer diameter and 0.5–0.75 mm wall thickness operated at temperatures up to 823 K and pressures up to 14 bar as an in situ plug flow reactors [38]. One advantage of the reported design is the possibility to directly measure the temperature of the catalyst bed since the reactor tube is thick enough to accommodate a thermocouple. The other advantage is that due to low X-ray absorption by the Be walls collection of XAFS data at photon energies below 5 keV is possible. The disadvantages lie in the chemical nature of the used beryllium (PF-60 grade Be contains up to 800 ppm Fe and other trace elements, which limits its application for certain catalytic reactions) and the toxicity of Be when oxidized which requires special care during handling [39]. To overcome the disadvantages of Be as reactor material Kispersky et al. reported the use of a vitreous carbon tube (glassy carbon, Fig. 6.7) as a robust relatively low-cost plug-flow in situ reactor [40]. With a 6 mm outer diameter and 4 mm inner diameter it is comparable to the reactors used in laboratory test rigs. The reactor was placed vertically for a down-flow operation which allowed spatially resolved XAFS measurements along the catalyst bed. The reactor can be heated to 823 K in oxidizing atmosphere and has been tested under pressures up to 25 bar. Both reactors of Bare [38] and Kispersky [40] were heated by means of an oven with openings for incoming and transmitted X-rays and as such can be used only for transmission XAS measurements.

High pressure studies (>20 bar) require special reactor designs as most of the X-ray window materials cannot withstand such pressure if made thin enough for low absorption of X-rays [41, 42]. Thus, the reactors and windows have to be reinforced. An example of a plug-flow reactor for transmission studies at high pressures (up to 150 bar) is shown in Fig. 6.8. The main body of the reactor is a

**Fig. 6.8** Schematic view of a transmission cell for catalytic studies at high pressure (up to 150 bar)



solid stainless-steel block with bored holes for gas (or liquid) inlet and outlet. The catalyst is placed in the middle channel of the reactor body and covered by graphite sealings and Be windows. Several sets of reactor covers and spacers allow different thicknesses of the catalyst bed. The assembled reactor is heated by a specially designed oven composed of two parts (Fig. 6.8) with a water- or air-cooled outer shell to prevent heating of beamline components and to achieve fast cooling if necessary.

## 6.3 In Situ Cell for Studies in Liquid Phase and at Elevated Pressures

Not all catalytic processes are realized in flow-through reactors. Some liquid-phase reactions and reactions in supercritical fluids require high pressure batch reactors to run [41]. Also, hydrothermal synthesis of catalysts requires autoclaves [43]. An in situ batch autoclave-like reaction cell was reported by Grunwaldt et al. [8]. This cell (Fig. 6.9) mimics a conventional autoclave with a polyether–ether–ketone (PEEK) inset with two beam paths, one in the middle of the cell to probe the liquid phase and one at the bottom to probe the solid catalyst. The total volume of the cell is about 10 ml and it is rated for pressures up to 150 bar. It is equipped with a magnetic stirrer and can be heated up to 473 K. This cell allows monitoring solid species at the bottom and soluble species in the liquid, which may be relevant for sample preparation by hydrothermal or solvothermal synthesis [44], investigation of heterogeneized complexes or Pd-catalyzed Heck-reaction [45, 46].

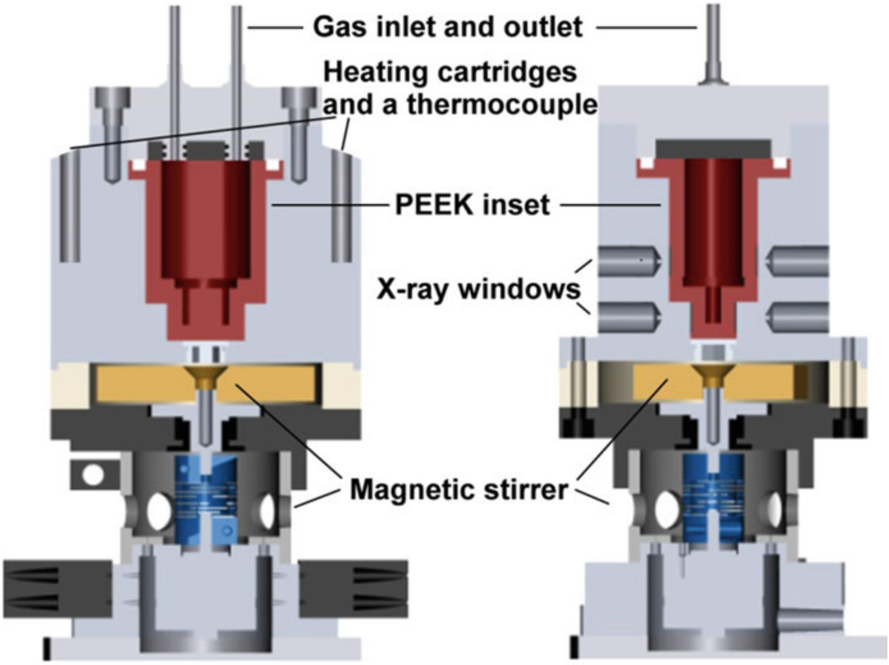


**Fig. 6.9** Scheme of an in situ batch cell for studies of liquids and liquid/solid interfaces at high pressures

## 6.4 In Situ Cell for Studies of Chemical Sensors

Sensors are another type of nanomaterials closely related to catalysts in terms of structure and gas–solid interaction (cf. Chap. 25). Therefore, as in catalytic studies, characterization of sensing materials should be carried out in a realistic gas atmosphere and at realistic temperatures. For semiconducting sensors an important difference is for example the sandwich structure of sensors which is typically a sandwich consisting of a sensing material, electrodes, a substrate and heater layers [47]. In case of noble metal doped $SnO_2$-sensors the strongly absorbing $SnO_2$-matrix and especially the only 50 μm thick screen printed layer for chemical sensors makes transmission XAS measurements difficult or impossible, and therefore, in situ cells optimized for fluorescence measurements are required. In addition to the cell design, the sensor itself should be fabricated in a way to avoid interference of fluorescence from the element of interest and heaters or electrodes, e.g., for studies of Pt-containing sensor materials Au electrodes and Au/Pd heaters can be used [47]. An in situ cell suitable for studies of sensors is depicted in Fig. 6.10 [48]. It consists of a gas tight vessel, sensor heater and readout connectors, large Kapton® windows, a sensor holder and gas ports. Although primarily designed for fluorescence measurements, X-ray windows on both sides of the cell allow transmission XAS to be recorded as well.

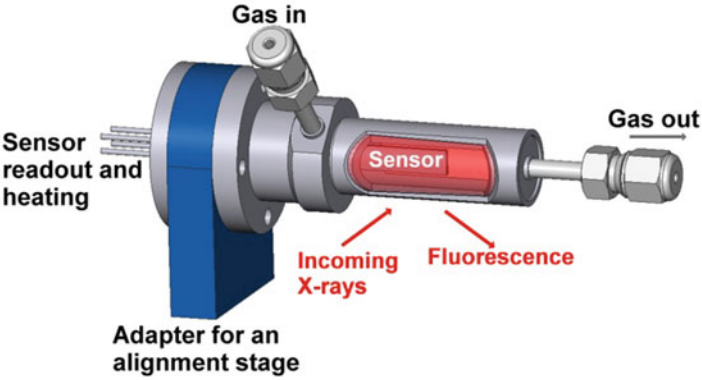


**Fig. 6.10** 3D drawing of an X-ray absorption/fluorescence cell for in situ and *operando* studies of sensors

## 6.5 In Situ Cells for Studies of Electrocatalysts

Unlike photocatalysts, electrocatalysts require specially developed cells for in situ and *operando* X-ray studies. The design concept of in situ electrochemical cells often reproduces real fuel cells and is based on a sandwich of electrodes. The anode and cathode are coated with the corresponding electrocatalysts and an ion (proton) conducting membrane. If the electrocatalysts to be studied are based on different metals, the only major modification required to adapt the fuel cell to in situ studies is to provide a thinning to serve as X-ray window [49, 50]. Some of the electrochemical cells do not require machining and can be built in the laboratory, e.g., an easy-to-build flexible electrochemical “coffee bag” type cell which is composed of a stack of metal and membrane foils in an aluminum bag with X-ray windows [51]. During the XAS experiment using the above mentioned cells, X-rays are transmitted through the whole fuel cell and in such a way anode and cathode materials are studied simultaneously. This works well when absorption edges of anode and cathode catalysts do not overlap, otherwise windows must be made in the anode and cathode layers to be able to study them separately as was done by C. Roth et al. who used a slightly modified commercial fuel cell as an in situ cell [52].

## 6.6 Conclusions and Outlook

The selected examples show that the combination of XAS and related photon-in/photon-out techniques with reaction cells operating close to realistic conditions provides a very powerful tool to establish structure–function relationships in catalysis and related areas. An appropriate design of spectroscopic cells is one of the keys to successful in situ and *operando* XAFS studies in gas and liquid phase or even under challenging high pressure conditions. Criteria which are typically applied in chemical engineering are valuable for an optimization of in situ cells for time-resolved and for *operando* studies. Reaction cell design will remain a very active field in future as one can only aim for the "best compromise" and the criteria described in this chapter may give a hint how to achieve this goal most rapidly. This will significantly contribute to a better understanding of the dynamics of functional materials, in particular the catalyst structure while monitoring the catalytic performance or even the kinetics of catalytic processes.

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