An *in situ* cell for small-angle scattering experiments on nano-structured catalysts

Jens Wenzel Andreasen,[a*] Ove Rasmussen,[a] Robert Feidenhans'l,[a] Frank Berg Rasmussen,[b] Robin Christensen,[b] Alfons M. Molenbroek[b] and Guenter Goerigk[c]

[a]Materials Research Department, Risø National Laboratory, P.O. Box 49, 4000 Roskilde, Denmark, [b]Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark, and [c]Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany. E-mail: jens.wenzel.andreasen@risoe.dk

The design, construction and operation of an *in situ* cell covering the temperature range from room temperature to 870 K with the sample in a controlled gas flow is demonstrated. The setup is designed specifically for acquiring small angle X-ray scattering data at the JUSIFA beam line at the Hamburger Synchrotronstrahlungslabor although it can be employed at other beam lines with only slight modifications. The cell is used for studying dynamic changes in size and morphology of nano structured catalyst particles.

Keywords: **SAXS; in situ; catalysis**

1. Introduction

During the last 10–12 years significant advances in studies of nano-structured catalysts have been achieved by implementation of new *in situ* experimental techniques using synchrotron radiation. Micro reactor cells have been constructed for use in X-ray diffraction (XRD) studies (Clausen *et al*., 1991) and X-ray absorption spectroscopy (XAS) (Clausen *et al*., 1994). Even combined XAS/XRD *in situ* methods have been employed (Grunwaldt *et al*., 2000). A natural continuation of these efforts is the incorporation of small angle X-ray scattering (SAXS) techniques to close the gap between the information on short-range atomic order provided by XAS and long range order as obtained from XRD. *Ex situ* small angle X-ray scattering is a well-established technique for studies of nano structured materials including catalysts (e.g. Matyi *et al*., 1987). *In situ* SAXS experiments have previously been described (Haubold *et al*., 1996; Haubold *et al*., 1999) but the developments presented here differ by utilising small capillary tubes that have been shown to approximate ideal plug flow micro reactors (Clausen *et al*., 1991).

2. Technical details

The *in situ* cell presented here (Fig. 1) is designed for, and operated at the B1 (JUSIFA) beam line at the Hamburger Synchrotron-strahlungslabor (HASYLAB). It is mounted on a 100 mm side entry flange on the main vacuum chamber at a position 196 mm from the standard sample holder position, closer to the monochromator. The cell is enclosed in its own small vacuum chamber that can be vented separately from the main chamber, allowing access to the micro reactor without disturbing the main chamber vacuum. The synchrotron beam passes through kapton foil windows in the inner chamber, which also has a Perspex™ window facilitating visual inspection of the micro reactor. The entire micro reactor setup with gas connections and heater element can be withdrawn on a sliding rail after venting the inner vacuum chamber. This design provides easy access to the sample environment in a natural working position, which is important because sample mounting requires delicate handwork when handling the fragile capillary tubes.

The heater element consists of a cylinder, manufactured from Macor® glass ceramic with a 0.5 mm deep, 1 mm steep helical groove into which a 0.4 mm diameter kanthal D resistance wire is wound (Fig. 1(***b***)). It is mounted in an aluminium crib, fixed with two aluminium cleats, a configuration that has proven mechanically stable over the entire temperature range. The heater wire has a specific resistance of 1.35 μΩm. According to specifications the Macor® ceramic is capable of withstanding a continuous working temperature of 1070 K. At least 870 K can be reached at the central position with this heater, requiring approximately 40 W electrical power. The temperature is measured with a NiCr-Ni thermocouple about 1 mm below the probed sample volume. This feedback provides input to a Eurotherm® temperature controller that regulates the power supply.

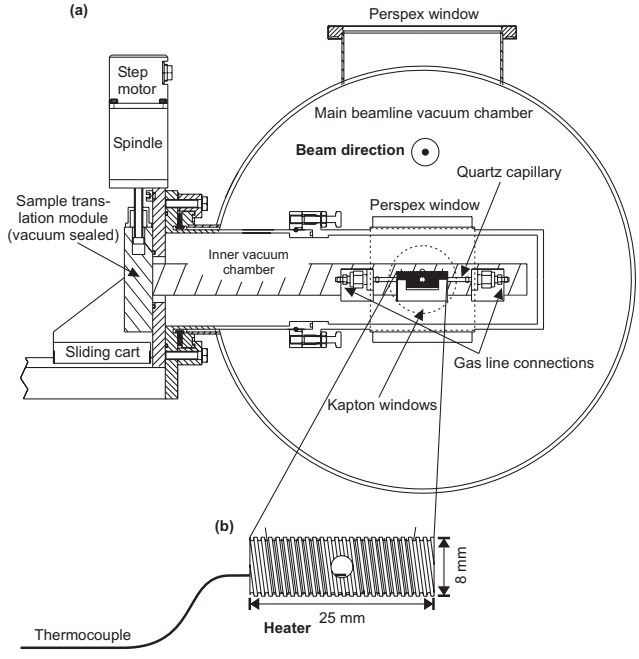

Figure 1 (***a***) View down the JUSIFA vacuum chamber/flight tube along the synchrotron beam direction, showing the inner vacuum chamber with the capillary micro reactor in measuring position. The entry points for gas and electrical current leads, thermocouple and vacuum pump connection are on the sample translation module in the left-hand part of the drawing. (***b***) Enlarged view of the heater element showing heater wire and central opening allowing beam passage. Also, the positioning of the thermocouple is shown.

The cell can be kept at a vacuum better than 0.1 Pa to reduce air scattering. At this pressure however, thermal conductivity is reduced by at least an order of magnitude. Therefore, when measuring at elevated temperatures, the *in situ* cell is flooded with a constant flow of helium to ensure temperature homogeneity. At the sampling position there is a temperature gradient along the micro reactor of 6 K/mm. The sampling position of the X-ray beam can be set with a precision of approximately ± 0.5 mm in the horizontal plane (parallel with the capillary) and better than ± 0.1 mm in the vertical plane. At 490 K the temperature is kept constant within ± 0.1 K.

The micro reactor itself consists of a 50–70 mm long quartz glass capillary tube, 0.5–2 mm in diameter with .01 mm thick walls (Markrörchen, Hilgenberg GmbH). During typical operating conditions a gas flow of 5–20 ml/min is passed over the catalyst

under a pressure of up to 2 MPa. The capillary is connected to the gas pipes with gastight Swagelok® fittings with graphite ferrules. Each ferrule is adapted individually to accommodate the small variations in capillary dimensions. This is accomplished by hand-drilling the ferrules for a snug fit. The heater assembly and gas connectors are mounted on a small optical bench allowing lateral adjustment with respect to each other.

3. Applications

As part of the commissioning, the calcination of a hydrozincite powder was followed. The 75–125 μm grain size fraction was loaded in a 1 mm diameter, 0.01 mm wall thickness quartz capillary and heated from 350 K to 570 K at a rate of 5 K/min. The sample was kept in a flow of 5 ml/min dry air. In the meantime, SAXS data were acquired at a rate of about 8 data sets per hour (Fig. 2).

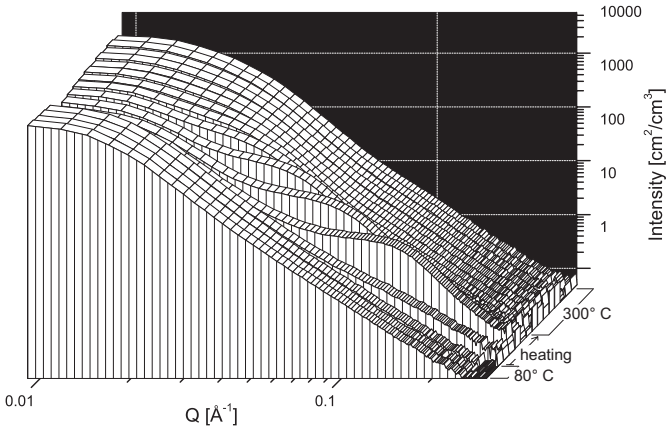

Figure 2 Calcination reaction in 5 ml/min flow of dry air.

Using the GNOM software (Svergun, 1992) and assuming a model of polydisperse spherical particles, a radius of gyration of 118.5 ±0.8 Å and 81.5 ±3.1 Å is derived for the uncalcined and the calcined sample respectively. It is clear however, that there is an intermediate stage of the reaction where much smaller particles are dominant (Fig. 3), information that is only accessible with *in situ* experiments.

The JUSIFA beam line at HASYLAB is designed to provide SAXS data on an absolute scale. Combined with the ability to tune the wavelength, this gives the possibility of performing contrast enhancing experiments by virtue of resonant X-ray scattering, known as ASAXS (see for example Haubold *et al.*, 1994), something which is particularly useful for studies of heterogeneous catalysts that represent three-phase systems consisting of metal, support and voids (Rasmussen *et al*., 2000; Polizzi *et al*., 2002). If, on the other hand, absolute intensities are not needed, regular SAXS experiments can be performed with a better time resolution.

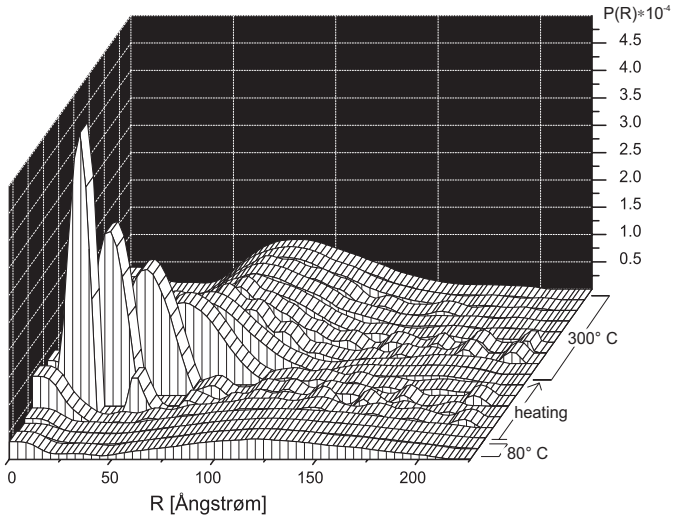

Figure 3 Size distributions as derived from the data shown in Fig. 2.

We gratefully acknowledge Steen Bang, Torben Kjær, Steen Nielsen, Carsten Gynther Sørensen, Rasmus G. Egeberg, and Dirk Hamann for valuable help during construction and comissioning of the cell. This work was supported by the Danish Technical Research Council, by DANSYNC, and by the European Commission under IHP-Contract HPRI-CT-1999-00040.

References

Clausen, B. S., Schiøtz, J., Gråbæk, L., Ovesen, C. V., Jacobsen, K. W., Nørskov, J. K. & Topsøe, H. (1994). *Tops. Catal.* **1,** 367-375.
Clausen, B. S., Steffensen, G., Fabius, B., Villadsen, J., Feidenhans'l, R. & Topsoe, H. (1991). *J. Catal.* **132,** 524-535.
Grunwaldt, J. D., Molenbroek, A. M., Topsøe, N. Y., Topsøe, H. & Clausen, B. S. (2000). *J. Catal.* **194,** 452-460.
Haubold, H. G., Gebhardt, R., Buth, G. & Goerigk, G. (1994). *Resonant Anomalous X-ray Scattering* edited by G. Materlik, C. J. Sparks & K. Fischer, pp. 295-304. Amsterdam: Elsevier Science B.V.
Haubold, H. G., Hiller, P., Jungbluth, H. & Vad, T. (1999). *Jap. J. Appl. Phys. Pt. 1* **38,** 36-39.
Haubold, H. G., Wang, X. H., Jungbluth, H., Goerigk, G. & Schilling, W. (1996). *J. Mol. Struct.* **383,** 283-289.
Matyi, R. J., Schwarz, L. H. & Butt, J. B. (1987). *Catal. Rev. - Sci. Eng.* **29,** 41-99.
Polizzi, S., Riello, P., Goerigk, G. & Benedetti, A. (2002). *J. Synchrotron Rad.* **9,** 65-70.
Rasmussen, F. B., Molenbroek, A. M., Clausen, B. S. & Feidenhans, R. (2000). *J. Catal.* **190,** 205-208.
Svergun, D. I. (1992). *J. Appl. Cryst.* **25,** 495-503.

 Received 29 August 2002 • Accepted 17 March 2003