JOURNAL OF CATALYSIS **118**, 79–84 (1989)

A High-Pressure Reaction Chamber for *in Situ* EXAFS Spectroscopy of Catalysts

THOMAS L. NEILS AND JAMES M. BURLITCH[1]

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received October 18, 1988; revised February 20, 1989

The construction of an X-ray penetrable reaction chamber, capable of withstanding operating conditions of 160°C and 68 atm has enabled the *in situ* EXAFS observation of a functioning copper and zinc oxide catalyst for methanol synthesis. X-ray transparent windows were fabricated from carbon fiber cloth and a high-temperature resin. The rate of methanol production from carbon monoxide, hydrogen, and carbon dioxide was monitored by gas chromatographic analysis of the cell effluent. The EXAFS study revealed a gradual disappearance of a Cu–O interaction while the hydrogen-reduced catalyst was producing methanol and indicated that the principal component of the working catalyst was highly dispersed Cu(O).

I. INTRODUCTION

Extended X-ray absorption fine structure (EXAFS) spectroscopy is now one of the major techniques used to study heterogeneous catalysts (*1–3*). Many of the EXAFS studies have been done at ambient conditions, and some investigations have been carried out under *in situ* conditions, i.e., conditions actually used during a catalytic reaction. The major obstacles to *in situ* measurements are the high temperatures and high pressures commonly used for heterogeneous catalytic reactions. High-temperature studies have been conducted with chambers incorporating windows of boron nitride (*4*) or beryllium (*5*), but neither of these cells was used with reaction pressures above 1 atm. A reaction cell constructed by Dalla Betta *et al.* (*6, 7*) has been shown to withstand pressures of 140 atm and temperatures of 437°C. This chamber employed beryllium windows that were kept at room temperature by water cooling and had an internal path length of 23 cm. When used under an atmosphere of 2% H_2S in H_2 at 70 atm, this path length was not detrimental because little of the beam was attenuated by the gases.

For the specific case of EXAFS analysis of Cu/ZnO catalysts for methanol synthesis, only Tohji *et al.* (*8*) and Clausen *et al.* (*9*) claimed to have carried out *in situ* studies. In both these investigations, however, no spectra were taken of systems that were actually producing methanol from synthesis gas. While Tohji and co-workers obtained spectra at temperatures appropriate for the catalytic reaction (100–200°C), no synthesis gas was present. This provided data from a reduced, activated catalyst, but it did not give information on a working catalyst. In the investigation by Clausen, the spectra were obtained at room temperature, after the catalyst had been subjected to normal reaction conditions. A study by Kau *et al.* (*10*) gave EXAFS spectra of activated and deactivated catalysts, but it was assumed that the production of methanol did not affect the structure of the reduced, activated catalyst. None of these investigations was carried out under the high pressures employed during the catalytic production of methanol (50–100 atm).

It has been implicitly assumed in most of the foregoing studies that the structure of the catalyst at ambient conditions is identi-

---

[1] Author to whom correspondence should be addressed.

0021-9517/89 $3.00

cal to the structure under the reaction conditions of high pressure and temperature. As shown by Klier, (*11*) the catalytic formation of methanol from $CO/H_2/CO_2$ over the Cu/ZnO catalyst is not a straightforward reaction. At 327°C, methanol is one of the least thermodynamically favored products of the hydrogenation of CO (*12*), and many years of study were necessary to develop the present-day, low-pressure (50–100 atm) catalysts. Because several of the by-products are thermodynamically more stable than methanol, the reaction must be carried out in fairly narrow temperature and pressure ranges (*13*). Changes in the nature of the active site may well accompany the changes in product composition as the conditions are varied. Prior to the present work there was no practical way to carry out EXAFS experiments on a Cu/ZnO system involving the use of X-ray-absorbing gas mixtures at high pressure.

We describe herein a reaction chamber capable of withstanding high pressure and temperature conditions, and preliminary results of its use to obtain truly *in situ* EXAFS spectra of working Cu/ZnO catalysts.

II. METHODS

The synthesis gas mixtures of $CO/H_2/CO_2$ (6%/71%/23%) and CO/H_2, as well as the mixture of N_2/H_2 (98%/2%), were obtained from Matheson. In all the gas mixtures, the H_2 and N_2 were 99.999% pure, while the CO and CO_2 were 99.99% pure.

All experiments were carried out at the Cornell High Energy Synchrotron Source (CHESS), which runs in a parasitic mode from the Cornell Electron Storage Ring (CESR). Preliminary studies of calcined catalysts were carried out in the C-1 and C-2 experimental hutches, while the *in situ* study was carried out in the A-3 hutch. Unless otherwise noted, ionization chambers filled with Ar or N_2 were used to monitor the incident X-ray beam and to detect the beam after it had passed through a sample. The beam energy was calibrated at 8.98 keV with copper metal foil.

Data analyses for EXAFS spectra were done using Kincaid's programs (*4*) on an DEC LSI-11-24 microcomputer. All difference spectra and integration of the resulting RDFs were carried out with LTPLOT, a locally developed data-analysis package running on a PRIME Model 9955 minicomputer; a commercial version of this data manipulation and plotting program, PLOT, is available from New Unit, Inc., Ithaca, New York.

Gas chromatograms were recorded on a Hewlett–Packard 5880A Gas Chromatograph with a 25-m cross-linked methyl silicone capillary column, a flame ionization detector, and a Level 4 5880A terminal. A solution of 0.5 ml of methanol, 5 ml of isopropanol, and ethyl acetate mixed in a 250-ml volumetric flask was used to calibrate the instrument for analysis by the internal standard method.

The reaction chamber was made of two 4¾-in. (1 in = 25.4 mm) stainless-steel UHV conflats joined face to face, with a window assembly bolted on the reverse side of each conflat (Fig. 1). One conflat was modified to include a gas inlet and a gas outlet. It also had a ½-in.-deep well in which a sample holder was placed and a 1⅛-in.-deep well for a thermocouple (Fig. 2). The other conflat had only a gas inlet added, as shown in Fig. 2. The two conflats were sealed with a copper ring gasket and were bolted together with case-hardened steel bolts.

A typical window assembly consisted of three layers, held together by a high-temperature adhesive (Aremco, type 526L). The central layer was made by coating two sheets of unsized, G105 Celion 3000K A carbon fiber cloth (Textile Technologies, Inc., Fairfax Station, VA) with the adhesive and pressing the sheets between two blocks of Teflon-coated aluminum. The coated fiber sheets were cured for 2 h at room temperature and then for 2 h at 92°C. These two sheets were then cut into 4.79-cm circles and glued together as a sandwich

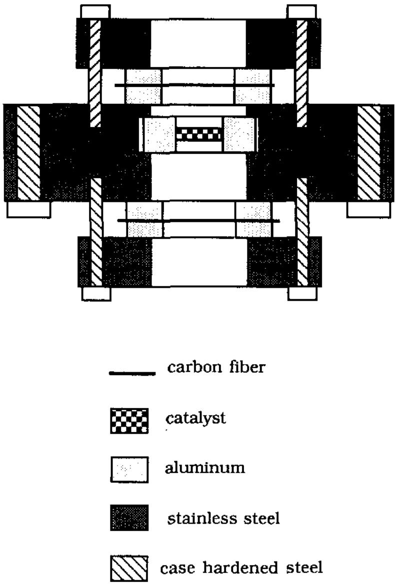

FIG. 1. High-pressure reaction chamber for EXAFS showing placement of windows and catalyst sample holder.

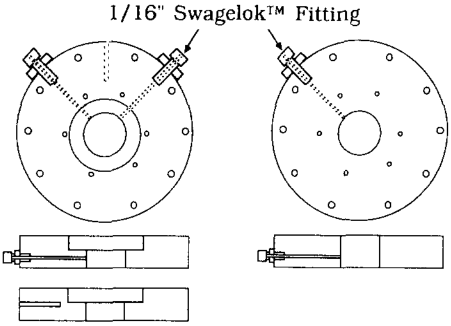

FIG. 2. Section and plan view of the modified UHV conflats showing passages for gas transport, sample holder, and thermocouple well.

with the weave of one sheet rotated 45° with respect to the weave of the other sheet. This sandwich was then cured in the same manner as the individual sheets. The window was strengthened by coating both sides with adhesive and curing at 92°C. This strengthening and sealing process was repeated three times.

An aluminum disk was placed on each side of the carbon fiber sandwich, which was 0.5–0.7 mm thick. The disks, used to support the fiber windows, were 0.4 cm thick, with an outside diameter of 4.79 cm. An oblong slit, 2.1 cm long and 0.63 cm wide, was centered in the disks as shown in Fig. 3. One face of the aluminum was smooth, while the other was roughened by sandblasting. A thin layer of adhesive was spread on the rough surface of the disks, the sandwich was coated on both sides with adhesive, and the three parts were pressed together. This window assembly was then bolted on to the conflat of the reaction chamber using a 2¾-in. blank conflat, cured for 2 h at room temperature, followed by 2 h at 92°C, and finally 16 h at 165°C. The internal X-ray path length of the assembled cell was 5 cm.

A sample holder that would both position the sample and allow synthesis gas to pass through it was fabricated out of aluminum (Fig. 4). The disk had an o.d. of 4.75 cm and an i.d. of 1.90 cm. A piece of the untreated carbon fiber was first placed into the threaded well, followed by a layer of the catalyst, and then another piece of untreated carbon fiber. A Teflon spacer was added on top, if necessary, and then a threaded aluminum ring was screwed into place to hold the sample. The chamber had an internal volume of 28.4 cm^3 and, with the

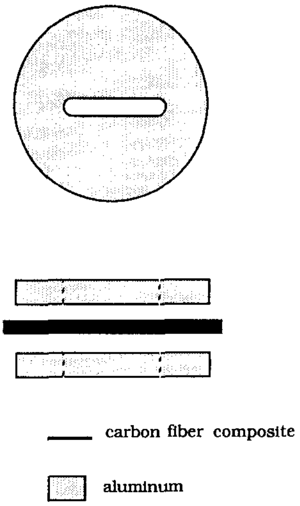

FIG. 3. Window support assembly.

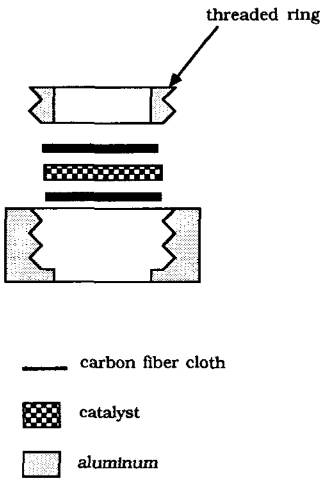

FIG. 4. Catalyst sample holder for high-pressure cell.

sample holder in place, an apparent dead volume of 11.7 cm^3. At a flow rate of 0.8 cm^3/s, approximately 40 times the cell's dead volume of synthesis gas was swept through the cell and through the collector in the 10-min data-collection period.

The reaction chamber was enclosed in a box constructed of Transite board with silicone rubber gaskets (Fig. 5). It had two electric cartridge heaters (Watlow, St. Louis, MO) that were controlled to ±2°C by an Omega CN5000 temperature controller, using a chromel/alumel thermocouple to monitor the temperature. There were two Mylar windows for the X-rays to pass through. The enclosure was made gas tight by sealing on the lid with silicone sealant and was flushed with a helium purge, using two gas ports. The enclosure was covered with aluminum-backed fiberglass insulation.

III. RESULTS

A preliminary test, at a beam energy of 8.98 keV, was conducted to find the overall attenuation effect of two composite windows and a sample holder containing two pieces of carbon fiber and 0.119 g of a CuO/ZnO (20/80) calcined catalyst precursor. The passage of the beam through these objects resulted in a total decrease in intensity from 21,000 cps at the monitor to 6252 cps at the detector, an acceptable drop in intensity.

For the *in situ* EXAFS reaction the chamber and oven were placed in the experimental hutch at CHESS, while the No. 3 cylinders of H_2/N_2 and $CO/CO_2/H_2$ were stored outside the hutch, with the latter cylinder stored in a vented box while in use. The synthesis gas regulator was equipped with an automatic shutoff valve (M. G. Industries), which was set to stop the flow of gas if it exceeded a flow rate of 1000 standard cm^3/min. The cylinders were connected to the reaction chamber by $\frac{1}{8}$-in. stainless-steel tubing. The gas leaving the reaction chamber was passed through a −78°C solvent trap to collect the methanol produced, and then to a hazardous gas vent in the hutch.

The sample holder was loaded with 0.120 g of CuO/ZnO (33/67), with two pieces of untreated carbon fiber supporting the catalyst powder. This holder was placed inside the reaction chamber, which was then attached to the gas delivery system. An initial check of the sample in the beam showed that the amount of catalyst and the positioning of the chamber were satisfactory for obtaining acceptable EXAFS spectra. A flow of N_2/H_2 (98/2) at 0.8 ml/s was begun

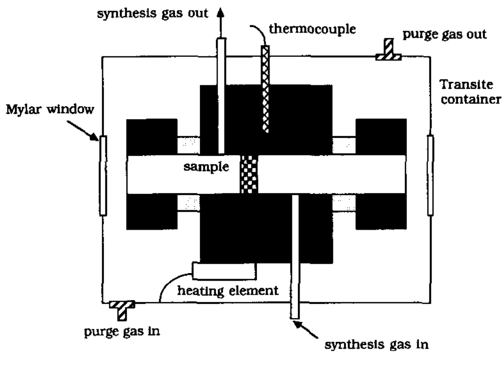

FIG. 5. Sketch of high-pressure EXAFS cell in the heating chamber.

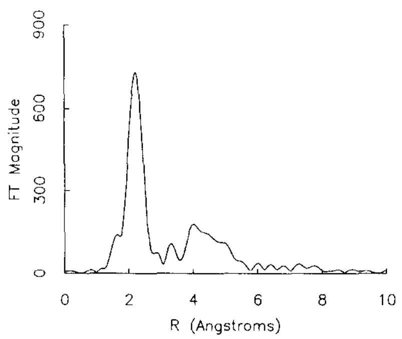

FIG. 6. Radial distribution function from Cu-EXAFS of reduced CuO and ZnO catalyst (30:70).

and the chamber was heated to 150°C. An example of the data taken periodically during this reduction phase is shown by the radial distribution function (RDF) in Fig. 6.

After 11 h, the N_2/H_2 was shut off and a flow of $CO/CO_2/H_2$ (24/6/70) gas was begun at a rate of 0.8 ml/s at 68 atm. The reaction was allowed to run in this manner for 23.5 h, with continual monitoring of the production of methanol. During this period, the average methanol production rate was $3.8 \pm 0.9 \times 10^{-3}$ kg/kg/h and remained essentially constant (within the limits of uncertainty). A typical RDF obtained during this stage of the reaction is shown in Fig. 7.

IV. DISCUSSION

Once preliminary studies showed that EXAFS spectroscopy could be used to study Cu/ZnO catalysts, a chamber that would allow for the investigation of the catalysts under actual reaction conditions was constructed.

The reaction chamber for this study had to fulfill three basic requirements. First, it had to hold up under temperatures of at least 150°C and pressures of 70 atm. Next, it had to allow X-rays to pass through both the chamber and the sample contained inside without greatly attenuating the beam intensity. Finally, the sample had to be positioned in the chamber so that the synthesis gas would pass through it, allowing the catalytic reaction to occur.

A simple and inexpensive design for the chamber body utilized two modified stainless-steel UHV conflats. The conflats were modified to include a recessed space to hold the sample, along with inlet and outlet holes for the synthesis gas. The two-part design allowed for easy access to the sample, yet provided a seal that would withstand the pressures involved in the reaction. Also, because the seal between the two halves was made with a copper gasket, the chamber could be used indefinitely by replacing the relatively inexpensive gasket periodically.

The most difficult portions of the chamber to construct were the two X-ray transparent windows. A carbon fiber composite was chosen as the window material. Carbon fiber cloth is permeable to all gases, though, and needed to be sealed in order to be gas tight. A high-temperature adhesive from Aremco (No. 526) was found to be a good sealant and was used to attach the fiber disk to two 0.5-cm-thick aluminum disks to provide extra support. The supports contained oblong holes approximately four times the height and twice the width of the X-ray beam at CHESS. The adhesive remained intact under 70 atm of pressure up to a temperature of 180°C, at which temperature the adhesive decomposed, causing leaks in the seal between the fiber and the aluminum supports. Leak

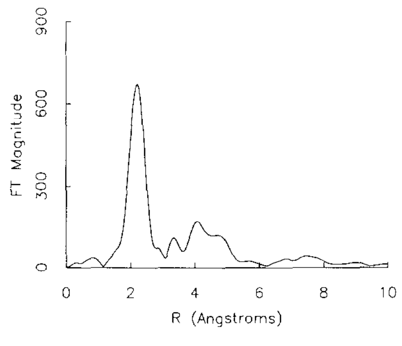

FIG. 7. Radial distribution function from Cu-EXAFS of a working methanol synthesis catalyst.

tests carried out at the normal operating pressure (68 atm) and temperature (160°C) showed that the isolated chamber did not lose pressure over a 12-h time period.

Prior to the final construction of the reaction chamber, tests were carried out at CHESS to investigate the attenuation of the X-ray beam by the entire group of objects in the chamber through which the beam would have to pass. These tests showed that 30% of the beam passed through the two windows, the catalyst sample, and the two pieces of untreated cloth, enough intensity to give meaningful data at normal beam intensities, even when the attenuation effects of the pressurized synthesis gas were included.

The reaction chamber had several limitations. It could not be heated above 180°C, and at this temperature could hold pressures no greater than 100 atm. Also, the windows were sensitive to thermal shock because they were assembled from materials of differing coefficients of thermal expansion. Thus, the chamber had to be heated and cooled slowly, a requirement not easily met under the severe time pressure at CHESS. For the experiments run in this study, though, under conditions of 160°C and 68 atm, the reaction chamber was completely operational after several heating and cooling cycles.

Spectra obtained from samples held in the chamber under *in situ* conditions were of similar quality to spectra obtained from samples at ambient conditions. The RDF of the reduced catalyst was similar to that of a reduced catalyst reported in earlier studies (*5*). The RDF of the working catalyst revealed that a further reduction of the catalyst occurs during the production of methanol under a $CO/H_2/CO_2$ atmosphere. Little if any Cu–O interaction was apparent in the RDF of the working catalyst; the dominant features are consistent with highly dispersed Cu(0) (*8*).

ACKNOWLEDGMENTS

The authors thank the Cornell Materials Science Center and the Department of Chemistry for financial support, and Textile Technologies, Inc., for gifts of carbon fiber cloth. We also thank the National Science Foundation for helping to provide facilities at CHESS and computer facilities in the Department of Chemistry. We appreciate the advice and support of Dr. Ning-Shih Chiu and the assistance, in numerous ways, of the staff at CHESS.

REFERENCES

1. Joyner, R. W., and Meehan, P., *Vacuum* **33,** 691 (1983).
2. Sinfelt, J. H., Via, G. H., and Lytle, F. W., *Catal. Rev. Sci. Eng.* **26,** 81 (1984), and references cited therein.
3. Lytle, F. W., Wei, P. S. P., Greegor, P. B., Via, G. H., and Sinfelt, J. H., *J. Chem. Phys.* **70,** 4849 (1979).
4. Lee, P. A., Citrin, P. H., Eisenberger, P., and Kincaid, B. M., *Rev. Mod. Phys.* **53,** 769 (1981).
5. Koningsberger, D. C., and Cook, J. W., *in* "EXAFS Spectroscopy, Techniques, and Applications" (B. K. Teo and D. C. Joy, Eds.), p. 412. Plenum, New York, 1980.
6. Dalla Betta, R. A., Boudart, M., Foger, K., Loeffler, D. G., and Sanchez-Arrieta, J., *Rev. Sci. Instrum.* **55,** 1910 (1984).
7. Boudart, M., Dalla Betta, R. A., Foger, K., Loeffler, D. G., and Samant, M. G., *Science* **228,** 717 (1985).
8. Tohji, K., Udagawa, Y., and Mizushima, T., Ueno, A., *J. Phys. Chem.* **89,** 5671 (1985).
9. Clausen, B. S., Lengeler, B., Rasmussen, B. S., Niemann, W., and Topsøe, H., *J. Phys.* **47,** 237 (1986).
10. Kau, C. S., Solomon, E. I., and Hodgson, K. O., *J. Phys.* **47,** 289 (1986).
11. Klier, K., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and Paul B. Weisz, Eds.), Vol. 31, p. 243, and references cited therein. Academic Press, New York, 1982.
12. Satterfield, C. N., "Heterogeneous Catalysis in Practice," p. 295. McGraw-Hill, New York, 1980.
13. Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1969.