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An Improved Sample System for the Infrared Study of Supported Metal Catalysts

Pressing silica-supported metal catalysts into self-supporting samples for IR transmission analysis often yields unpredictable results. The insulating properties of the sample make it difficult both to control and to measure the sample temperature, and the fragile nature of the sample adds to the difficulty of temperature measurement. Pressing the sample material at high pressures increases the sample's strength and improves the sample's transmittance; however, it reduces the rate of gas-diffusion into the interior of the sample (*1*), producing a nonuniform concentration of the adsorbed gas throughout the sample.

Typically, self-supporting samples are heated in an oven section of the sample system, either by radiation heating in vacuum or by convection heating in an inert gas. Cooling the sample to room temperature is accomplished by waiting for the slow radiation cooling in vacuum or by purging the system with the inert gas. The arrangement described in this paper allows the sample to be heated and cooled in vacuum by external means with the sample temperature measured directly.

Two improved sample arrangements have been described in the past few years. In one, the self-supporting sample is pressed onto a molybdenum screen (*2*). In the other, the sample is pressed directly onto the tungsten screen (*3*). In both cases, the screen is heated resistively with an electric current. The sample arrangement described here uses some of the features of these systems and also has the capability to cool the sample quickly and to cool it below the ambient temperature.

The sample system described here was devised to enable us to obtain the infrared transmittance spectrum of adsorbed species on silica-supported metal catalyst samples. The sample is pressed so as to embed the tungsten screen that is clamped between two copper rings. The rings are fastened to a heavy copper rod that can be heated or cooled by means external to the vacuum system. Embedding the tungsten screen into the sample has several advantages:

(1) The thermal conductivity of the tungsten wires, which are in intimate contact with the pressed silica, permits temperature control of the insulating sample.

(2) The sample's increased mechanical stability allows us to routinely prepare thin samples for use where the low infrared transmittance of the silica is a problem.

(3) The mechanical support of the embedded screen permits a thermocouple to be inserted directly into the sample, either for direct sample temperature measurement or for a calibration that relates the sample temperature to the temperature of the support rings.

(4) The mechanical support of the screen allows a stable sample to be formed by pressing at lower pressures. Such a sample allows for faster diffusion of the gases into (and out of) the sample interior.

Figure 1 shows the screen mounted between two OFHC copper rings. The screen is notched to match the screw holes and the thermocouple channel and then pressed flat, prior to assembly. Circular and radial grooves are machined into the clamping surfaces of the rings to eliminate trapped gases.

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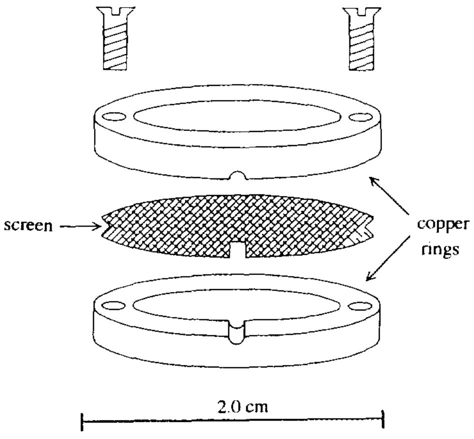

FIG. 1. Schematic drawing of copper rings and screen assembly.

The sample is pressed between two steel pistons. The lower piston fits inside the copper rings and the screen assembly is supported so the screen is just above the face of the piston. With sample material on both sides of the screen, the upper piston is lowered onto the sample material and the sample is pressed.

We have used several ways to insert a thermocouple into the sample. The following procedure was used for the data shown in this paper. After the sample was pressed, a small hole (1/32″ diameter) was drilled through the center of the sample and screen. The thermocouple junction is placed in the hole with the leads passing across the surface of the sample and through the thermocouple channel in the copper rings. The hole is filled with additional sample material and pressed again. To ensure that the thermocouple wires are not shorted (*4*), by contact with the screen, after the second pressing they are pulled away from the sample surface until their only contact with the sample is with the thermocouple junction at the center of the sample. The thermocouple wires now extend from the center of the sample, through the thermocouple channel to electrical feedthroughs on the vacuum flange that supports the entire sample system.

Another thermocouple is spot-welded to a thin layer of silver on one of the copper rings of the sample-holder assembly (*5*). After calibration of the sample temperature, this thermocouple may give adequate temperature information so that it is not necessary to insert the thermocouple into the center of each sample disc.

Figure 2 shows a drawing of the sample-holder assembly to which the mounted screen is attached. The assembly is machined from an OFHC copper rod. The mounted screen is held against a vertical face of the assembly with screws. This assembly forms the bottom of a well that passes through the vacuum flange and is open to the outside of the system. The upper part of the well is a stainless steel pipe, silver-soldered to the copper. The pipe passes through and is welded to the UHV flange whose lower surface mates with a flange on the vacuum system. Because the flange also carries the electric feedthroughs for the thermocouple wires, the entire sample system can be removed by removing this one flange.

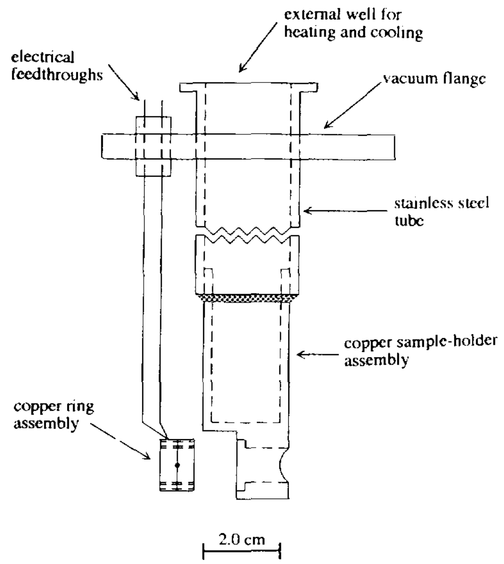

FIG. 2. Schematic drawing of sample-holder assembly.

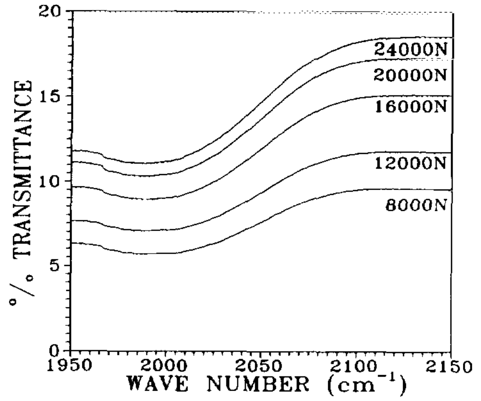

FIG. 3. Transmittance effects for a 16-mg silica sample, 13 mm in diameter, pressed with various forces (N).

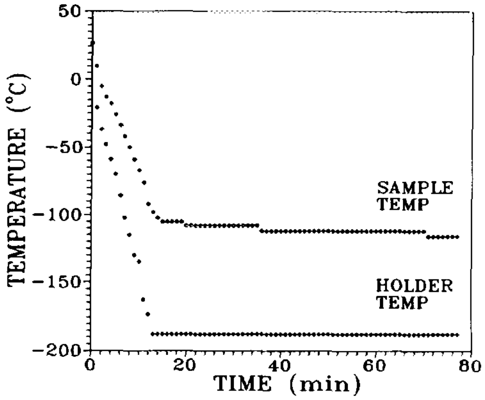

FIG. 4. Sample and copper ring temperatures when the sample is cooled externally with liquid nitrogen.

Sample heating is accomplished by lowering an electric cartridge heater into the well. Cooling is accomplished by circulating liquid nitrogen through the well.

Figure 3 shows the infrared transmittance of a pressed, silica sample. The sample is 13 mm in diameter and 16 mg in weight. The tungsten screen, by itself, has a transmittance of 90%. The transmittance is further reduced both by the intrinsic absorption of the silica and by scattering of the silica powder. As the sample is pressed at higher pressure, the thickness of the sample is reduced, the voids between the silica particles are reduced in size, and the transmittance of the sample increases. Figure 3 shows a difference in the transmittance by a factor of two for usable samples pressed at different pressures.

The sample is processed by a standard O_2 and H_2 cleaning procedure (*6*). This treatment sometimes changes the relation between the two measured temperatures (the sample temperature and the sample-holder temperature) on a new sample assembly, presumably because the process changes the thermal conductivity of the contact between the screen and copper rings and/or the copper rings and the sample-holder assembly. After the cleaning procedure, however, the temperatures are quite reproducible. Figure 4 shows the two temperatures as a function of time when liquid nitrogen is circulated in the well. The sample reaches a temperature of −100°C after about 12 min and then slowly drops to a minimum temperature of about −120°C.

Figure 5 shows the temperature as a function of time when a constant voltage is applied to the cartridge heater. For the voltage used here, the maximum sample tempera-

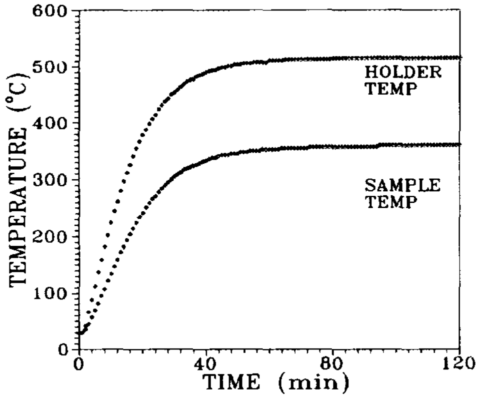

FIG. 5. Sample and copper ring temperature when the sample is heated with an electric cartridge heater.

ture is about 350°C and it takes about 30 min for the temperature to rise to 270°C.

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