Simple transmission infrared cell made of Swagelok for in situ infrared spectroscopic studies of heterogeneous catalysis

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2 AUTHORS, INCLUDING:

Masaharu Komiyama

University of Yamanashi

Simple transmission infrared cell made of Swagelok for *in situ* infrared spectroscopic studies of heterogeneous catalysis

Masaharu Komiyama and Yoko Obi
Department of Chemistry, Yamanashi University, Takeda, Kofu 400, Japan

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A transmission infrared (IR) cell of a very simple design for *in situ* study of heterogeneous catalysis is constructed using commercially available parts. The cell design is based on the use of Swagelok unions, and the use of custom-built parts is minimized. The use of a sheathed thermocouple as an internal local heater of the sample eliminated the window cooling lines up to 300 °C sample temperatures, making the cell design very simple and also resulting in short heating and cooling time of the sample. The usefulness of the cell in studying heterogeneous catalysis is demonstrated in the *in situ* observation of catalytic NO_x removal. © *1996 American Institute of Physics.* [S0034-6748(96)02204-9]

I. INTRODUCTION

Infrared (IR) spectroscopy is a powerful tool for *in situ* study of heterogeneous catalysis,[1] and numbers of IR cells designed specifically for this purpose have been built.[2] Most of these designs involve custom building the most, if not all, of the parts, which makes building such cells costly and time consuming, particularly where in-house glass and/or machine shops are not available.

In this article, we report a construction of a simple IR cell using commercially available parts. While custom parts have not been completely eliminated, their number has been greatly reduced, and at the same time the cell design became very simple. Its usefulness in studying heterogeneous catalysis *in situ* is demonstrated.

II. IR CELL DESIGN

A. Main body and window assembly

For the main body of the IR cell, we chose to use a Swagelok union tee. This choice is due to the fact that for a transmission IR cell at least three ports are necessary: two coaxially aligned ports for the IR beem to pass through, and the third port as a feedthrough for thermocouple, gas, and others. For this purpose a union cross that has four ports may also be employed, with two ports to be used as feedthroughs. Figure 1 shows a schematic illustration of the IR cell constructed. The prototype cell employs $1\frac{1}{4}$ in. Swagelok tee. Detailed explanation for each of the parts follows.

Two coaxially aligned ports of the tee are to be used for the IR beam path, and thus IR windows have to be placed in them. Since the present cell was to be used under *in situ* conditions, gas-tight sealing was necessary. This was accomplished by using O rings. Figure 1 shows the cross section of one port with an IR window in its place.

The back ferrule (2) placed in the Swagelok nut (1) holds a viton O ring (3) which keeps the IR window (4) from directly contacting the metal parts. A cut steel pipe (5) is placed inside of the union tee. The pipe is tapered on one side so that it holds an O ring (3) which is also in contact with the inner wall of the tee and the IR window thus constituting the gas-tight sealing. The whole window assembly may be tightened by turning the nut (1) to the desired strength.

B. Feedthrough assembly

The design of the feedthrough assembly may depend on the specific individual experimental requirements. If only gas exchange is necessary, a Swagelok heat exchange tee, which is a combination of a standard union tee and a bored-through reducer through which a process tube is inserted, may be connected to the third port of the union tee and the cell is complete. The heat exchange tee can accommodate two inlets: gas inlet and outlet, or one may replace its process tube with sheathed thermocouple and connect the remaining inlet to vacuum line.

If the experiment requires more than two inlets, there may be two solutions: one is to use a union cross instead of a union tee. Then two ports are available as feedthroughs which may provide, for instance, thermocouple, heater and

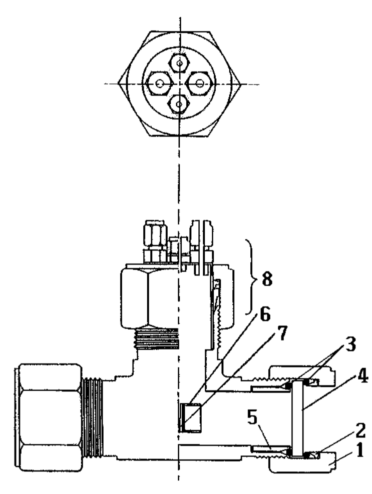

FIG. 1. Schematic of the IR cell. The cross section is shown on the right half. (1) Swagelok nut, (2) back ferrule, (3) O ring, (4) IR window, (5) cut and tapered pipe, (6) sample holder, (7) sample, and (8) feedthrough assembly (see next section).

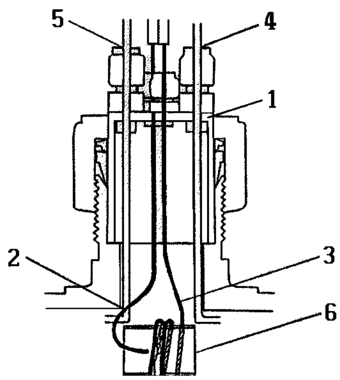

FIG. 2. The cross section of a custom-build feedthrough fit into a Swagelok union tee (cf. Fig. 1). (1) A metal pipe with one end weld sealed, (2) thermocouple, (3) heater, and (4) gas inlet, and (5) outlet. Sample holder (6) is supported by the heater.

gas inlet and outlet by connecting a heat exchange tee to each port. If the IR spectrophotometer in use does not allow placing an union tee in its sample compartment, and the experiment requires more than two inlets, one may have to custom build a feedthrough. A design of a feedthrough that accommodate four inlets to be fit in one port of a Swagelok union is shown in Fig. 1, and in more detail in Fig. 2. Here a metal pipe (1) with one end weld sealed is constructed. On that welded end bored-through Swagelok unions or male connectors for thermocouple, heater, and gas inlet and outlet ports are screwed in and welded.

C. Temperature control

In the present cell design heating of the sample was done internally, so as to avoid heating the whole cell which has a large heat capacity. Such a design has two advantages: firstly, the internal and local heating of the sample would require less power, and thus fast heating is possible compared to the heating of the entire cell. Since heating is limited to a small area around the sample, cooling is also expected to be fast. Secondly, since the heating is limited to only the local area and the heat capacity of the main cell body is very large, IR windows will not be affected by the heating up to a certain temperature. This eliminates the necessity of window cooling lines which is customary for externally heated IR cells.[2]

As a heater a sheathed thermocouple was employed. A sheathed thermocouple is very convenient for several reasons. First, they come in a variety of sizes (diameter and length), and hence it is very easy to obtain one with the necessary heating power. Second, they are electrically well insulated. Third, it occupies only one inlet union, compared to two in the case of a heater (sheathed or not sheathed) which has two ends. Furthermore, they are compatible with most of the *in situ* catalytic reaction conditions. In the present design the heater also serves as a sample holder support, as may be seen in Fig. 2(3). For sample temperature measurements another sheathed thermocouple (2) is placed near the sample, as shown in Fig. 2.

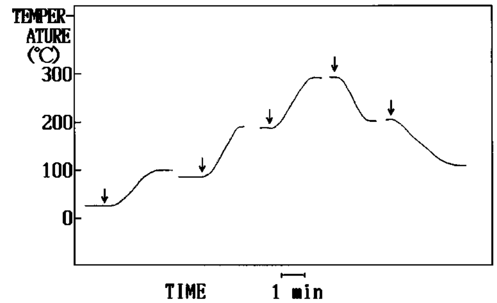

FIG. 3. The time course of sample heating with a 1/16-in.-diam, 40-mm-long sheathed chromel-alumel thermocouple under PID control with a maximum applied voltage of 10 V. Arrows indicate the points where temperature settings were stepwise changed.

III. PERFORMANCE OF THE IR CELL

The IR cell that has been built following the above design was tested for *in situ* study of catalytic NO_x conversion. Titania (P-25, Nippon Aerosil Co.) was used as a sample catalyst. A 13-mm-diam titania wafer weighing approximately 20 mg was placed in the sample holder, and the cell was purged with Ar gas. In the Ar stream the thermal characteristics of the present cell was examined and the results are shown in Fig. 3. Arrows in the figure indicate the points where temperature setting were changed stepwise. In the present cell the heater is a 1/16-in.-diam, 40-mm-long stainless-steel-sheathed chromel-alumel thermocouple. Under PID control with 10 V maximum voltage application, the sample was heated from room temperature to 100 °C within 2 min. Further 100 °C step increases were also accomplished within 2 min each. Temperature decreases were also performed in a similar time scale as may be seen in Fig. 3. Such fast temperature response is very rare with IR cells made of metal, and demonstrates the merit of this design incorporating internal local heating.

At 300 °C gas flow into the cell was switched to NO, and then to a $NO+C_2H_4$(1:1) gas mixture, and the resulting spectra were recorded. Nitrogen oxide reduction by hydrocarbons is a prospective automobile exhaust control reaction.[3] Figure 4 shows the background-subtracted spectra. Peaks attributable to gas-phase NO at about 1900 cm^{-1} and

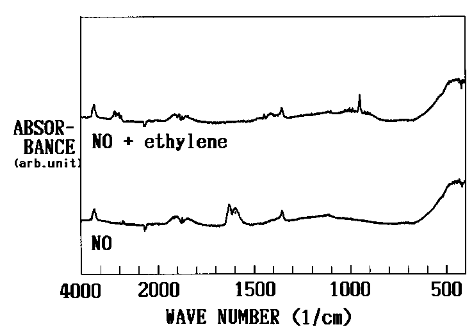

FIG. 4. IR spectra of titania taken under NO or $NO+C_2H_4$(1:1) gas mixture at 300 °C. Background spectra taken under Ar atmosphere at the same temperature has been numerically subtracted.

C_2H_4 at about 950 cm^{-1} are visible, which are due to the rather high concentration of each gas. When C_2H_4 is not present in the gas (lower spectrum) a peak attributable to adsorbed nitrate species is apparent at about 1600 cm^{-1}. The introduction of C_2H_4 at 300 °C eliminates this peak (upper spectrum), indicating the reactive removal of the adsorbed nitrate species from the catalyst surface. This removal of the surface nitrate by C_2H_4 was not observed below 250 °C.

In the present study only a simple atmospheric reaction was examined using this ''Swagelok'' IR cell. Nevertheless, since the gas-sealing parts of the cell are Swagelok ferrules and O rings, it should withstand certain level of subatmospheric and vacuum conditions. The attainable vacuum level may be limited by the Swagelok seals and/or IR window sealings. Furthermore, since the cell is entirely made of stainless steel except the IR windows, it should also withstand high-pressure conditions. In this case the limiting parts are most likely to be the IR windows. Strengthening the IR windows may be accomplished by using harder window materials such as CaF_2 instead of soft NaCl if the observation wavelength is satisfactory, by making the open diameter of the window smaller by building a smaller cell, or making the window thicker.

[1] L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic, London, 1966).
[2] J. B. Peri, in *Catalysis-Science and Technology*, edited by J. R. Anderson and M. Boudart (Springer, Berlin, 1984), Vol. 5, Chap. 3.
[3] M. Iwamoto, N. Mizuno, and H. Yahiro, in *New Frontiers in Catalysis*, edited by L. Guczi, F. Solymosi, and P. Tetenyi (Elsevier, Amsterdam, 1993), Pt. B, p. 1285.