

An Improved Infrared Cell Reactor for Use in Transient Response Studies: The Catalytic Oxidation of CO Reexamined

Recent advances in rapid scan infrared spectroscopy have revived an interest in *in situ* transient response studies in catalysis. Several excellent designs have appeared in the recent literature (1-3). However, the requirement of combining a small dead space cell volume reactor essential for transient response studies with single-pass differential flow capabilities has not yet been met. In order to meet these requirements, an infrared cell-reactor should conform to the following: (1) the residence time in the infrared cell-reactor should be less than the time required for scanning the spectrum; (2) the reactant gases should preferably be forced through the sample disk with little or no leakage around the edges; (3) the outlet from the infrared cell-reactor should be properly interfaced with a gas chromatograph or another suitable analytical measuring device such as a quadrupole mass spectrometer; and (4) the cell should be constructed to handle adequate heating schedules. The combination of requirements 1, 2, and 4 has been difficult to meet. In a previous paper, Miura and Gonzalez (2) published a design capable of meeting requirements 2, 3, and 4. However, the volume of the cell-reactor was 60 ml rendering it useless for transient studies or for use as a pulse microreactor. Hicks *et al.* (3) on the other hand, have published an excellent design for an infrared cell-reactor having a very small volume. However, it could not be used as a single-pass differential reactor. In this paper we report on a new design which combines the features of the design published by Miura and Gonzalez (2) and that of Hicks *et al.* (3). We will also consider the catalytic oxidation of CO over Pt/

SiO₂ to illustrate the transient capabilities of the infrared cell-reactor.

The design of this new infrared cell-reactor is shown in both Figs. 1 and 2. It was constructed by the Byron Lambert Co. of Franklin Park, Illinois. It was machined directly from a No. 304 stainless-steel bar.

The cell dimensions and assembly are shown in Figs. 1 and 2, respectively. The total reactor-cell volume was 2.5 cm³. A flow rate of 100 ml/min can be achieved without difficulty yielding an average residence time in the reactor of 1.5 s. The polycrystalline CaF₂ optical windows were sealed to the cell using Grafoil gaskets provided by the Union Carbide Corporation. The sample cell holder was secured in the cell by means of a notched retainer ring. The catalyst sample was inserted into the sample holder using a unique pressing assembly which, except for the dimensions, was identical to that reported in Ref. (2). The system was secured by means of stainless-steel screws and gaskets prepared from asbestos fiber. Heating was accomplished using an external annular copper split block stove. The optical windows could be cooled using an external water supply. The water was circulated through circular channels machined directly into the stainless-steel assembly. The sample temperature was monitored by means of a second thermocouple pressed against the sample disk calibrated against an external thermocouple.

The reactant gases were forced directly through the sample disk with little or no leakage around the edges of the sample. Because of this design, a gas chromatograph or a quadrupole mass spectrometer located downstream of the reactor could be used to

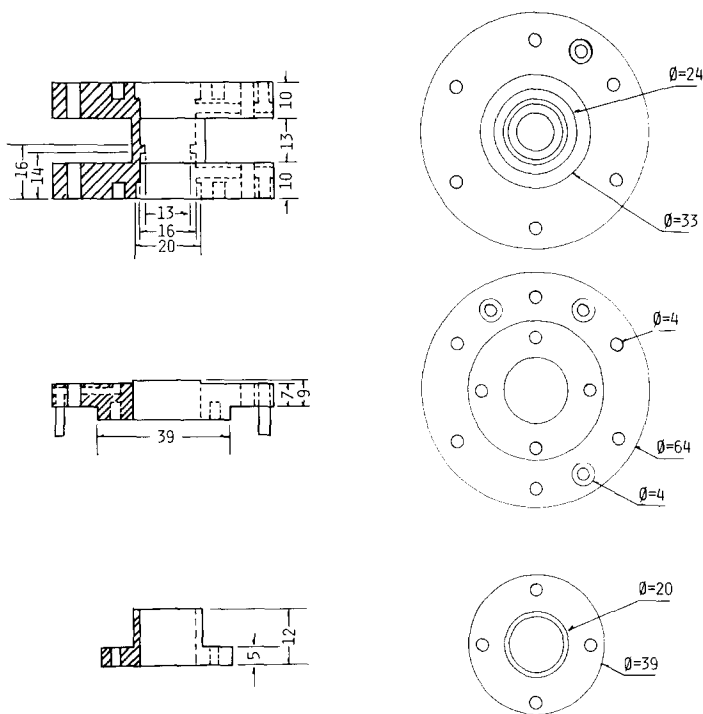


FIG. 1. Infrared cell-reactor. Dimension unit: mm.

measure reaction rates. The small reactor cell volume also enabled use of the cell as a pulse microreactor which could be used to make chemisorption measurements and measure surface areas by the dynamic pulse method (9). A maximum temperature

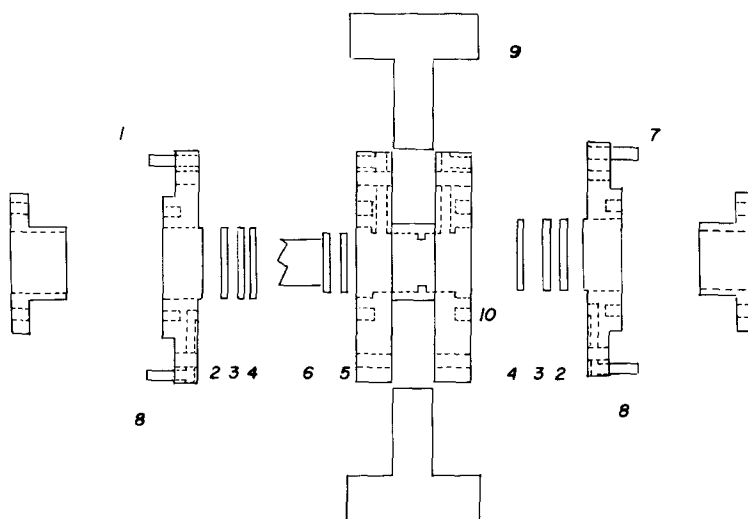


FIG. 2. Infrared cell-reactor assembly: 1, gas inlet; 2, asbestos fiber gasket; 3, optical window, CaF_2 , 2 cm, \times 0.15 mm; 4, Grafoil gasket; 5, sample holder; 6, notched retainer ring; 7, gas outlet; 8, water port; 9, copper stove split block; 10, water cooling channel.

of 473 K without cooling water and 573 K with cooling water, could be attained without incurring damage to the optical lenses.¹

The Catalytic Oxidation of CO

The transient response capabilities of the infrared cell-reactor described above were tested using the catalytic oxidation of CO as a reaction probe. The mechanism of this reaction is reasonably well understood (4–7) and is thought to proceed by a Langmuir–Hinshelwood mechanism involving the reaction between a chemisorbed CO molecule and an oxygen atom. At large CO/O₂ reactant gas ratios the surface is covered by a monolayer of CO. However, at temperatures in excess of 473 K, the adsorption of CO and oxygen becomes competitive (8). The silica-supported samples used in this study were prepared by coimpregnation. Initially enough H₂PtCl₆ · 6H₂O (Strem Chemical) to give a nominal Pt loading of 1% Pt/SiO₂ was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. The solutions were mixed with Cab-O-Sil, Grade M-5 (Cabot Corp., Boston, Mass.) until a slurry was formed. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The dried catalyst was then ground into a fine powder before use. The powdered catalyst was pressed into self-supporting disks using the special pressing assembly. The disks had an optical density of 0.2 mg mm⁻². Following reduction in H₂ at 573 K, the metal dispersion was obtained by the dynamic pulse method (9) and found to be 30%.

Catalyst pretreatment was as follows: the catalyst was heated in flowing He for 2 hr at 373 K. The temperature of the catalyst was then increased from 373 K to 573 K in flow-

ing He at 2 K/min and then treated in dry air at 573 K for 2 hr. The catalyst was then cooled to 473 K in flowing He. The gases used in this study were research grade or better and were purified by standard purification techniques. The gas flow rates of the catalyst treatment and transient study were maintained at 24 ml/min.

The results of this study are summarized in Fig. 3. Five spectral regions were scanned and the absorbance was plotted as a function of time. The frequency windows were chosen to coincide with the R and the P branches of gaseous CO₂ (2358–2362 and 2339–2343 cm⁻¹), the absorption frequency of adsorbed CO on Pt (2072–2080 and 2090–2094 cm⁻¹), and the absorption frequency of CO chemisorbed on oxidized Pt (2119–2123 cm⁻¹). The infrared spectrum was scanned at 1-s intervals using a Nicolet 60SX spectrophotometer equipped with a mercury cadmium telluride detector. The resolution of the spectrometer at this scan speed was 4 cm⁻¹. The data were processed using the associated Nicolet IR-80 data system.

When the helium carrier gas was replaced by 5% CO/He, the infrared band due to chemisorbed CO (2070–2094 cm⁻¹) was observed to increase. Simultaneously, the infrared band due to V₃, the antisymmetric stretching frequency of CO₂, was also observed to increase. When 5% O₂/He was added to the reactant gas mixture a sharp increase in the absorbance of the CO₂ band was observed. Simultaneously the infrared band due to chemisorbed CO was observed to decrease. After a 10-s interval, the reaction reached steady state. The infrared band due to chemisorbed CO reached its maximum absorbance while the absorbance of the band due to CO₂ rapidly fell to zero. It is interesting to note that when 5% CO/He was introduced, the increase in the absorbance of the CO₂ band was considerably sharper than that due to CO. The possibility that this is due to adsorbed CO₂ must be excluded for the following reason: (1) the heat of adsorption of CO₂ on Pt is less than

¹ Further details on the construction of this cell can be obtained by writing to Richard D. Gonzalez, Professor and Head, Department of Chemical Engineering, The University of Illinois at Chicago, Box 4348, Chicago, Ill. 60680.

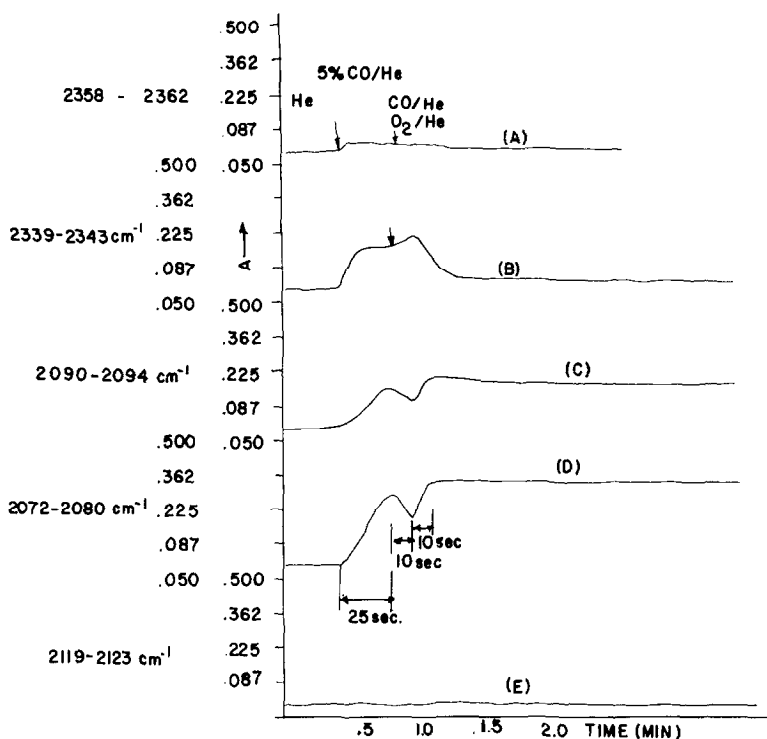


FIG. 3. Infrared spectra of chemisorbed species. (A) R branch of CO_2 , (B) P branch of CO_2 , (C) and (D) chemisorbed CO, (E) CO chemisorbed on oxidized Pt sites.

20.9 kJ/mole (10). Assuming a frequency factory of 10^{-13}s^{-1} , one can estimate a desorption rate of about $5 \times 10^{25} \theta$ in units of molecules $\text{cm}^{-2}\text{s}^{-1}$. If we ignore internal transport, the absolute upper limit on the rate of CO_2 production when the 5% CO gas mixture is exposed to the oxygen covered surface is set by the collision frequency of CO which is about 2.3×10^{23} . Equating these two rates and solving for θ , one obtains a surface coverage of 5×10^{-3} which is probably overestimated by at least an order of magnitude. This surface coverage of CO_2 is insufficient to account for the rather large intensity of the CO_2 band observed in the transient response spectrum.

What then is the origin of the 10-cm^{-1} red shift in the CO_2 absorption frequency? A calculation based on 40 mg of 1% Pt/SiO₂ having a dispersion equal to 30% could yield about 0.01 cm³ of gas at 473 K. This could give substantial short-term CO_2 gas pressures in a disk of thickness 0.05 cm.

The suggestion that the observed 10-cm^{-1} red shift is due to vibrationally hot CO_2 cannot be excluded. Brown and Bernasek (11) have shown that CO_2 molecules can survive thousands of collisions and still yield a red shift in the infrared spectrum. The superposition of several excited states removes the doublet structure associated with the P and R branches of the ground state as observed in the present study.

Following the attainment of a steady state CO_2 reaction rate, the absorbance of CO_2 rapidly falls to zero. For this reason, we must assume that the intense CO_2 absorption band is due to a transient response induced by the initial desorption of a relatively large volume of CO_2 . When CO_2 was passed over a pure Cab-O-Sil wafer, no detectable CO_2 was observed.

In conclusion, we feel that the infrared cell-reactor outlined in this paper will be useful to researchers who wish to study the formation and disappearance of short-lived

surface transients under *in situ* catalytic conditions. In addition, the present design can also be used to measure actual reaction rates while simultaneously probing the structure of surface species using spectroscopic techniques.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also wish to acknowledge the support of the National Science Foundation who provided funds for the purchase of the FTIR spectrometer used in this research under Grant CHE-8216482. We would like to thank Professor Bell who was kind enough to send us a copy of the blueprint used in his infrared cell design. We are also grateful to Professor Haller for stimulating discussions on the possible origin of the CO₂ red shift.

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Received January 6, 1986