JOURNAL OF CATALYSIS 95, 21–32 (1985)

Cylindrical Internal Reflectance: A New Method for High-Pressure *in Situ* Catalytic Studies

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Received July 12, 1984; revised March 7, 1985

Cylindrical internal reflectance using crystals embedded into well-stirred high-pressure autoclaves was developed as a new technique for *in situ* infrared studies of a variety of catalytic reactions. The technique demonstrated several advantages for *in situ* analysis permitting the direct infrared observation of catalytically active intermediates which were not previously observable. Examples of a variety of high-pressure homogeneous metal-catalyzed reactions, coordination complex reactions, zeolite syntheses, and heterogeneous catalyst analyses are presented to demonstrate the unique advantages of the technique at autogeneous conditions. Spectral data are presented for reactions operating up to 1500 psi (10.3 MPa) and 150°C for methanol catalyzed carbonylation by cobalt and rhodium, cobalt–ruthenium-catalyzed carbonylations, and ZSM-5 zeolite synthesis. The technique was found to be useful for several other catalytic reactions and for the study of the reactions of coordination complexes used as homogeneous catalysts.

INTRODUCTION

A new *in situ* method for the infrared analysis of chemical reactions has been developed which permits the direct observation of reaction intermediates generated by a process operating under normal high-pressure and high-temperature conditions. The method utilizes the principle of cylindrical internal reflectance (CIR) and has been incorporated into the design of several high-pressure reactors for the study of catalytic and other reactions under autogeneous conditions. A comparison of this technique to other high-pressure *in situ* infrared cells based on infrared transmission optics has demonstrated a definite superiority of the cylindrical internal reflection reactors. Our study on the mechanisms of several catalytic reactions, organometallic synthesis and zeolite synthesis using the reactors which were fabricated has provided mechanistic details previously unattainable.

Optical System

The application of cylindrical internal reflection in chemical process control and the cylindrical internal reflection crystal element for these analyses was first conceived by Wilks and co-workers (*1*, *2*). The optical and mechanical design of the optical bench required for laboratory infrared analysis was first reported by Sting and Wilks (*3*). A horizontal double pass internal reflection method to measure the infrared spectra of liquids was described earlier by Harrick (*4*) and the measurement of liquids by ATR was reported by several groups (*5–7*). The scope of analysis by various internal reflectance spectroscopic (IRS) methods has also been reviewed by Harrick (*8*).

The basic cylindrical internal reflection cell used in these studies is illustrated in Fig. 1 and used an internal reflection crystal fabricated from ZnS, ZnSe, Si, Ge, sapphire, or any other optically transparent material which has high mechanical strength, is resistant to thermal shock, and is not chemically attacked by the reaction media. The crystal was fabricated into a polished cylinder with 45° conical ends. The high-pressure reactions reported here

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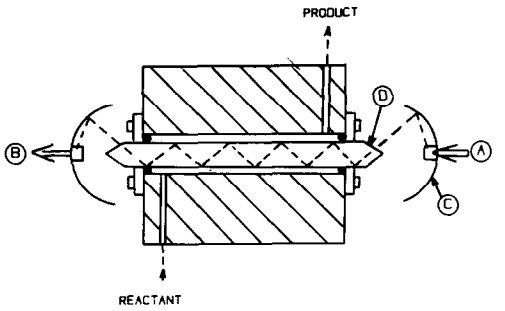

FIG. 1. Cylindrical internal reflectance crystal of Barnes Analytical Design (Barnes CIRCLE cell) (*3*). (A) incident infrared beam, (B) emitted beam directed toward detector, (C) focusing mirrors, and (D) cylindrical internal reflectance crystal of either ZnSe, ZnS, Si, or Ge.

utilized elements which were 3.25 in. long having a diameter of 0.25 in. The optical bench attachment used the design developed by Barnes Analytical-Spectra Tech (*9*). In this design seen in Fig. 1 the infrared beam was directed into a set of convex cone mirrors and a toroidal mirror where the energy was focused onto the 45° angle of the CIR element. As the beam passes through the crystal, ten internal reflections occur at the sampling surface before it exits the crystal and is redirected toward the detector by another set of mirrors. At each point of reflection at the crystal, the penetration depth into the surrounding solution is around 1 to 1.5 μm affording a total cell pathlength of only 10–15 μm. A Nicolet 60SX Fourier-transform spectrometer equipped with a sensitive (MCT-B) detector was utilized in these studies.

High-Pressure Reactor Cells

The high-pressure cells which were fabricated for the *in situ* catalysis studies were designed for the study of three basic types of reactions. A low-volume flow-through cell shown in Fig. 2 was appropriate for plug flow experiments. The magnetically stirred autoclave shown in Fig. 3 was found to be adequate for the study of the stoichiometric reactions of coordination compounds in solutions where a reacting gas was not required or for static zeolite synthesis. The optimum reactor for the study of well-mixed homogeneous catalytic reactions or slurry catalyst reactions involving a reacting gas in a liquid media of the catalyst is shown in Fig. 4. The direct-drive, well-stirred batch reactor shown in Fig. 4 utilized the standard top portion of a Parr Mini Reactor (*10*). The bottom was fabricated from 316 stainless steel and was equipped with an $\frac{1}{8}$-in.-thick Teflon liner shown in Fig. 5, part B. For certain applications involving corrosive reacting media, a stirrer fabricated from Teflon was used. Usually, a solid Teflon insert was used for most reactions to reduce the internal gas volume out of safety considerations. A high-pressure locking device for the cylindrical internal reflectance crystal is also shown in Fig. 4 and used a Teflon O-ring. Higher-tempera-

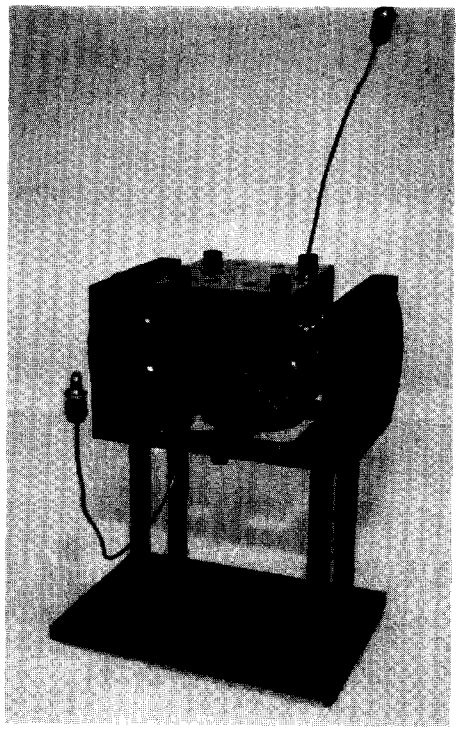

FIG. 2. Plug flow reactor equipped with thermostated heating block, high-pressure gas inlet and effluent lines, high-pressure crystal closure mounted on Barnes CIRCLE optical bench (*3*).

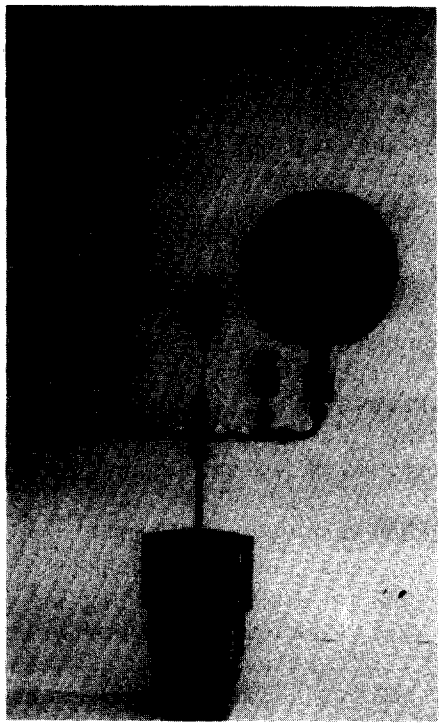

FIG. 3. Magnetically stirred high-pressure autoclave equipped with an embedded cylindrical internal reflectance crystal, high-pressure gauges, and valves with a Teflon-coated magnet for agitation. Reactor equipped with cartridge heaters and a controlling thermowell as well as a measuring thermocouple in the solution.

ture reactions require other specially designed O-ring materials.

All of the 316 stainless-steel reactors (*6*) were static tested at 125 atm (12.6 MPa) while being heated at 150°C. They have been used in numerous catalysis experiments under autogeneous conditions of 80 atm (8.11 MPa) and 50 to 160°C.

Several other high-pressure infrared cells for *in situ* catalytic studies have been described in the prior literature; most of these were based on transmission techniques. Studies at very high pressures were recently examined in a system reported by Vidal and Walker (*12*) for studying ethylene glycol synthesis. This system is typical of several transmission cell designs (*13, 14*) in that the catalytic reaction was carried out in an external high-pressure autoclave and a small portion of the reactor contents were

FIG. 4. Parr Mini Reactor head with embedded cylindrical internal reflectance crystal. Reactor equipped with direct-drive stirrer, Teflon liner, and high-pressure facilities.

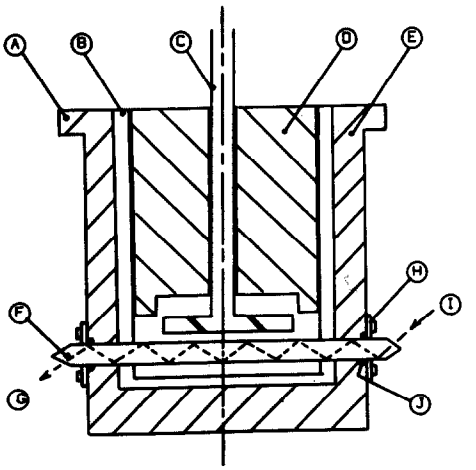

FIG. 5. Schematic of bottom of well-stirred autoclave (cylindrical internal reflectance reactor) shown in Fig. 4. (A) 316 Stainless-steel machined body, (B) ¼-in. Teflon liner, (C) direct-drive stirrer, (D) solid cylinder of Teflon to reduce internal volume, (E) high-pressure closure to connect with standard head section of a Parr Mini Reactor, (F) cylindrical internal reflectance crystal, (G) emitted infrared beam from crystal, (H) high-pressure closure for crystal, (I) focused infrared beam onto crystal at 45° angle, and (J) Teflon O-rings.

periodically flowed through a high-pressure transmission cell. Previously Morris and Tinker (*15*) used such a cell to examine the rhodium-catalyzed hydroformylation reaction. A modification of this technique continuously recirculates the reactor content under pressure from the autoclave, into the cell where the solution is returned to the autoclave. The optimum design for such a recirculation, transmission cell appears to be the design of Rigby, Whyman and Wilding (*16*) who utilized an internal recirculation design with a short recirculation length. The transmission cell reported by King and King (*17*) used an internal recirculation technique without transfer line. A flat plate transmission–reflectance cell was previously utilized by Rossiter (*18*) which in principle could be used for high-pressure studies. The capability for the measurement of liquids using various internal reflectance spectroscopic techniques was previously reviewed by Harrick (*4*). The present study shows that the particular geometry of the cylindrical internal reflectance crystals used in these experiments afford several unique advantages for *in situ* analysis when they are configured into high-pressure autoclaves as described in the following section.

ADVANTAGES OF REACTOR STUDIES USING EMBEDDED CYLINDRICAL INTERNAL REFLECTION CELLS

The CIR high-pressure reactors demonstrated several capabilities which are enumerated here. Support for each claim will be given by experiments described in subsequent sections.

(1) The well-stirred reactor shown in Fig. 4 provided an instantaneous view of the transition metal complex intermediates and products under conditions which were at steady state and well mixed with respect to the optical element. This facility was demonstrated by a set of experiments where a known initial concentration of methyl acetate in methanol was integrated using the Nicolet FTIR software. Then successive amounts of methyl acetate were directly added to the solution; the spectral scans were started after 1–2 sec and measured over 15 sec. Subsequent scans and integration of the methyl acetate band at various times over 3–5 min at each stage showed constant concentration measurements and that each solution had come to equilibrium with the CIR crystal faster than one could measure the spectrum.

Several catalytic experiments operating at autogeneous conditions demonstrated that a rapid modification of the reaction conditions resulted in a change in the observable catalytic intermediates within the time period of 1–2 min required to obtain high-quality spectra.

(2) The quantitative analysis of reaction products and coordination complex intermediates in strongly adsorbing solvents was easy to perform. A calibration study using 12 different methyl acetate concentrations between 0.02 and 50 v/v% in methanol in the high-pressure CIR cell resulted in a linear absorbance versus concentration relationship with a correlation coefficient of 0.9994.

(3) Since the pathlength does not change at high temperatures and pressures using the CIR technique, quantitative data over a wide range of conditions were accurately and readily obtained. The integrated intensity of methyl acetate in 15% concentration measured at both 1 and 80 atm were different by only 0.08%. Neither high temperatures nor pressures affected pathlengths in CIR type measurements. Small changes in the integrated intensities of solutes were observed as a function of change of refractive indices of the crystal and organic media. These were normally small. Our studies generally used calibration mixtures which were measured under typical temperatures and pressures as a precaution.

(4) The *in situ* reactors discussed here offer a degree of mixing of gas and solution components which is typical of that in a Parr Mini Reactor (*10*) since the geometries of the two vessels are very similar. Since the stirred solution is also constantly in di-

rect contact with the CIR crystal, the method is advantageous for the *in situ* study of gas–catalyst–solution reactions.

(5) The reactors shown in Figs. 3 and 4 were equipped with $\frac{1}{8}$-in.-thick Teflon liners ensuring the absence of artifacts resulting from metal contact with corrosive reaction solutions.

(6) This new method is the only *in situ* IR method available for the study of gas–liquid–solids or catalyst slurry reactions under well-stirred conditions. An example of a zeolite synthesis illustrates this capability in a subsequent section.

(7) The reactions were easy to run and permitted easy alteration of conditions in the reactor. The latter capability permitted the observation of rapidly reacting intermediates by adjustment of the reaction conditions. In certain reactions, such as the Monsanto acetic acid process discussed later, specific intermediates were not observable when the reaction was carried out under standard process conditions, but could be observed by modest alterations in the reaction conditions.

CATALYTIC STUDIES USING CYLINDRICAL INTERNAL REFLECTANCE

Extensive studies in these laboratories have demonstrated that high-pressure reactors with embedded cylindrical internal reflectance elements provide mechanistic information on a wide range of reactions relating to the catalytic sciences. Complete details of these studies will be reported later on in individual publications. The objective of this report is to describe the equipment used in high-pressure CIR-FTIR analysis and to show key experiments which illustrate the qualities of the CIR method as an *in situ* spectroscopic technique.

Ruthenium-Modified Cobalt-Catalyzed Carbonylation of Methanol to Methyl Acetate

The ruthenium-modified cobalt-catalyzed carbonylation of methanol to form methyl acetate (*19*), shown in Scheme 1, will be presented here in some detail to illustrate the level of scientific information which may be gained from the method.

$$2CH_3OH + CO \xrightarrow{\text{Ru–Co Complex}} CH_3CO_2CH_3 + H_2O$$

SCHEME 1

This reaction will also be used to demonstrate specific capabilities of the high-pressure CIR reactors as an FTIR *in situ* method. Figure 6 illustrates that (1) high-quality *in situ* spectra of a metal-catalyzed reaction may be obtained at high pressures (1200 psi; 8.27 MPa) and 150°C; and that quality spectra could be obtained in a strongly absorbing solvent like methanol. The spectra in Fig. 6 were taken at 4 cm^{-1} resolution by averaging 500 scans which required a total analysis time of 7 min. Curve A in the figure shows the cobalt-alone-catalyzed reaction, and Curve B shows the ruthenium–cobalt catalyzed reaction at equal reaction times of 250 min. The cobalt concentration in Figs. 6–8 was 0.10 *M* and the ruthenium concentration was generally 0.02 *M*. The product, methyl acetate, appeared as a single band absorbing at 1736 cm^{-1}.

To illustrate the capabilities of the well-mixed, stirred autoclave in Fig. 4 to yield a

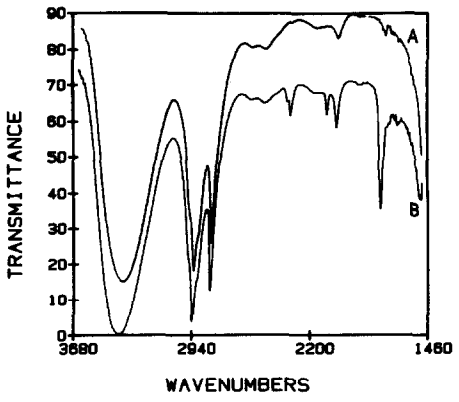

FIG. 6. Reaction of methanol and carbon monoxide at 1200 psi (8.27 MPa) and 150°C after 250 min reaction time using cobalt iodide catalyst (Curve A) and cobalt iodide–ruthenium chloride trihydrate catalyst (Curve B). All spectra were recorded at a resolution of 4 cm^{-1} using 500 averaged spectra without any smoothing.

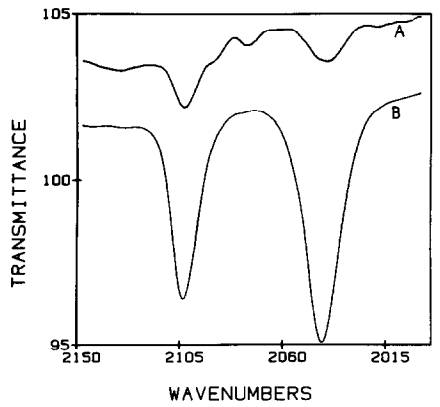

FIG. 7. Cobalt–ruthenium catalyzed conversion of methanol and CO to methyl acetate at 1200 psi (8.27 MPa) and 150°C. Curve (A) reaction mixture pumped at 1200 psi from a standard Parr Mini Reactor through an external low-volume infrared CIRCLE cell shown in Fig. 2. (B) Reaction mixture analyzed directly using cell shown in Fig. 4. Both spectra are recorded at identical intensities and used identical pathlengths.

true instantaneous view of reaction intermediates under autogeneous conditions, the infrared spectral data for the metal carbonyl region in the ruthenium-modified cobalt-catalyzed carbonylation of methanol are presented in Curve B of Fig. 7. The figure also illustrates the intensities of bands in Curve A measured for the same methanol carbonylation reaction when the reaction was carried out in a separate autoclave and pumped through a 3-ft × $\frac{1}{16}$-in. transfer line to the flow-through infrared cell shown in Fig. 2. The solution was recirculated under 1200 psi (8.27 MPa) pressure using a pump rate of 110 ml/hr at a linear liquid velocity of 6 cm/sec. The stirred case (Curve B) and externally recirculated case (Curve A) were recorded at the same spectral intensities and identical pathlengths. The two reactions were run under identical conditions and both spectra were taken at the same reaction time.

A comparison of these data shows that an important catalytic intermediate absorbing in the infrared at 2035 and 2104 cm^{-1} was partially decomposed by the time that it was pumped to the infrared cell using the former technique. Larger differences were observed in the cobalt carbonyl-catalyzed homologation of methanol. This loss in intensity, potentially leading to a misinterpretation of spectral information, likely resulted from an instability of the intermediate due to the lack of efficient gas–liquid mixing in the transfer line and external infrared cell. In other cases involving the sequential formation of reaction intermediates, spectral information may be lost due to the further reaction and disappearance of the intermediate before it reaches the externally located infrared cell. The intermediate appearing at 2035 and 2104 cm^{-1} was identified as $[Ru(CO)_3I_3]^{-1}$ (*20*) and its role in the reaction will be briefly described below. This comparison points out the truly *in situ* nature of catalytic experiments using the cell shown in Fig. 4, and calls attention to potential problems with other types of *in situ* studies using high-pressure infrared cells located external to the high-pressure reaction device.

An illustration of the type of scientific information obtainable using reactors with embedded cylindrical internal reflectance crystals is shown in Fig. 8. Curves A, B, and C were all obtained at 150°C and 1200

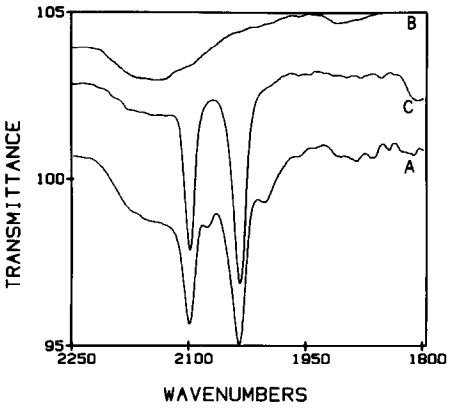

FIG. 8. Reaction of methanol and carbon monoxide at 1200 psi (8.27 MPa) and 150°C using cobalt iodide catalyst (Curve B); using ruthenium trichloride trihydrate catalyst (Curve A); and using a cobalt iodide and ruthenium trichloride catalyst (Curve C).

psi (8.27 MPa) of carbon monoxide using methanol solutions of (A) a ruthenium iodide catalyst alone, (B) cobalt iodide alone, and (C) a ruthenium–cobalt iodide catalyst. The strong band appearing at 1736 cm^{-1} (Fig. 8) was identified as the product methyl acetate; dissolved CO_2 appeared at 2341 cm^{-1}, $[Ru(CO)_3I_3]^{-1}$ appeared at 2035 and 2104 cm^{-1}, $[Co(CO)_4]^{-1}$ appeared at 1900 cm^{-1}, and no other discrete bands were observed for another cobalt complex. Carbon monoxide appeared as a broad absorption between 2000 and 2250 cm^{-1}. Figure 6 showing the mid-infrared spectra for the cobalt-alone-catalyzed carbonylation reaction in Curve A and the ruthenium-modified cobalt-catalyzed carbonylation system in Curve B, taken at equal reaction times of 250 min, demonstrates the outstanding effect of ruthenium to co-catalyze the rate of methyl acetate production at low pressures (*18*) as shown by the differences in intensity of the 1736-cm^{-1} product acetate bands. Separate experiments using the iodide form of the ruthenium catalyst alone produced no methyl acetate after 250 min. All of the spectra demonstrate the capability of this method to obtain instantaneous concentrations of products and intermediates for use in kinetic analyses.

Our data suggest that the effect of ruthenium, illustrated in Fig. 6, in the form of the ruthenium complex, $[Ru(CO)_3I_3]^{-1}$, solely functions to run the water–gas shift reaction to produce hydrogen to reduce CoI_2 to HI and to keep the water concentration in the reactor at a low level. It was previously demonstrated (*18*) that the low-pressure cobalt-catalyzed homologation system maintained high rates when the reaction was maintained anhydrous and afforded low rates if the water of reaction was permitted to react with the cobalt catalyst. To demonstrate that hydrogen generation was necessary for the carbonylation reaction, a CIR reactor experiment was run in which 20 psi of hydrogen was initially pressurized into the cobalt-alone-catalyzed reaction along with 1200 psi of carbon monoxide. The product development, followed by IR showed that the rate of methyl acetate formation was much faster than the cobalt-iodide-catalyzed reaction without added hydrogen. The cobalt-iodide-alone reaction under just CO pressure eventually produced methyl acetate after a long induction time.

Other experiments whose intermediates and products were followed by IR were a series of reactions at a fixed Co to Ru ratio while the methyl iodide concentration was varied over a wide range. The simultaneous observation of the $[Ru(CO)_3I_3]^{-1}$ bands, the $[Co(CO)_4]^{-1}$ band, and the rate of product formation showed that only the $[Co(CO)_4]^{-1}$ was slightly reduced in intensity while the rate of methyl acetate formation increased linearly as the methyl iodide concentration was increased.

In situ stoichiometric studies showed that the stoichiometric reaction of $[Co(CO)_4]^{-1}$ with methyl iodide rapidly formed cobalt iodide and acetyl cobalt tetracarbonyl which reacted only slowly at ambient temperature, but rapidly at 60°C to form methyl acetate. The *in situ* analyses on this reaction as well as our homologation studies have in no case detected the complex $[RuCo_3(CO)_{12}]^{-1}$ postulated (*21*) as the active intermediate in these reactions. Naturally, the absence of this intermediate in the spectra does not rule it out as an active intermediate if its lifetime is very short. A detailed presentation of our spectral and kinetic data and several other series of experiments relating to the mechanism of this reaction will be described elsewhere. However, we currently conclude that (1) the main reaction is one between $[Co(CO)_4]^{-1}$ and methyl iodide; (2) hydrogen is necessary in low concentrations to convert the intermediate cobalt iodide to HI which reforms CH_3I upon reacting with methanol; and (3) the ruthenium component runs the water–gas shift reaction which provides the low concentration of hydrogen necessary to maintain the reactions.

Rhodium-Catalyzed Carbonylation of Methanol to Acetic Acid

Since the cylindrical internal reflection technique is a short pathlength method, it was felt that it would permit the analysis of the Monsanto acetic acid process in an acetic acid–methanol solvent. Prior studies (*22*) utilized a heptanoic acid–methanol solvent system in a transmission cell to avoid blanking out the metal carbonyl region by the strongly absorbing acetic acid–methanol mixture.

Our experiments in the well-stirred reactor (Fig. 4) used a 50% acetic acid solution in methanol–water using a catalyst prepared from rhodium trichloride trihydrate (0.011 *M*) and an excess of methyl iodide. The catalyst study was performed at 150°C and 600 psi (4.138 MPa) of carbon monoxide and is shown in Fig. 9. These spectra are presented to illustrate the spectroscopic point that the CIR method permits the IR analysis of reactions in even strong absorbing solvents.

A typical infrared spectrum of the rhodium carbonyl absorption region taken at these conditions is shown in Fig. 10. The principal intermediate $[Rh(CO_2)I_2]^{-1}$ appeared at 1989 and 2061 cm^{-1}. It was interesting to note that bands resulting from dissolved carbon monoxide appeared in our spectra as a low-intensity, broad-band adsorption between 2045 and 2225 cm^{-1}. The pressurization of 1200 psi (8.278 MPa) of carbon monoxide over methanol at room temperature or at 150°C independently showed this low-intensity absorption.

An examination of the reaction in pure methanol using a rhodium–methyl iodide catalyst permitted the observation of the rhodium acyl complex for the first time under autogeneous conditions. Curve B in Fig. 11 shows the infrared spectrum of the active catalyst system with bands at

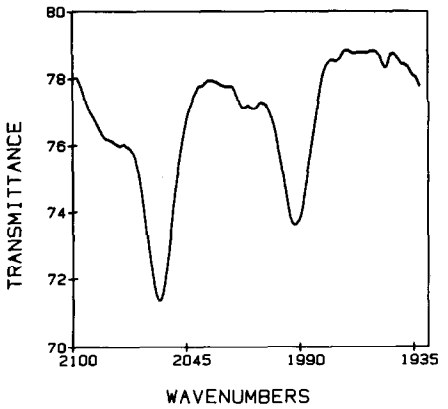

FIG. 10. Rhodium carbonyl region showing $[Rh(CO)_2I_2]^{-1}$ in reaction of CO with CH_3OH at 600 psi, 150°C in methanol, water, acetic acid solvent using a rhodium trichloride hydrate–methyl iodide catalyst.

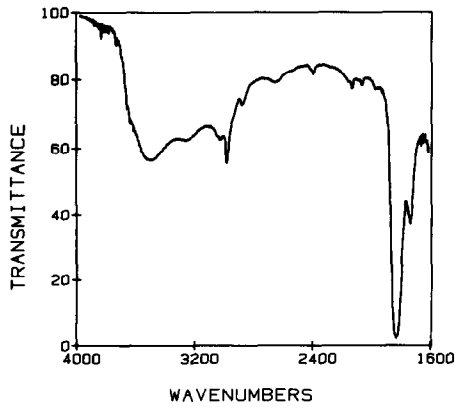

FIG. 9. Carbonylation of methanol to acetic acid at 600 psi CO and 150°C using a $RhCl_3 \cdot 3H_2O$—CH_3I catalyst in 46% CH_3OH, 51% CH_3CO_2H, and 3% v/v H_2O.

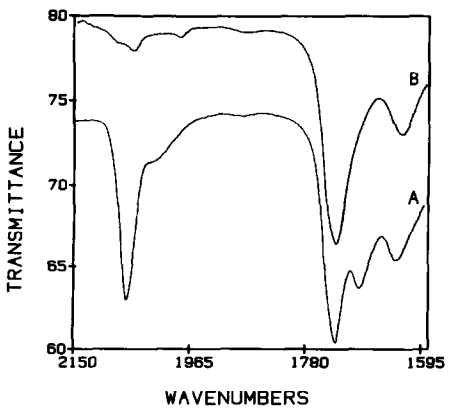

FIG. 11. Reaction of CO with pure methanol at 360 psi (Curve B) and 320 psi (Curve A) at 150°C using a $RhCl_3 \cdot 3H_2O$—CH_3I catalyst in both cases.

2061 and 1989 cm^{-1} for $[Rh(CO)_2I_2]^{-1}$ and for the product methyl acetate at 1736 cm^{-1}. When the CO pressure was permitted to decrease through consumption by the reaction, the $[Rh(CO)_2I_2]^{-1}$ complex vanished from the reaction to be replaced by a strong band at 2066 and 1699 cm^{-1} seen in Curve A. These bands were assigned to a five coordinate rhodium acyl complex $[Rh(CO)(COCH_3)I_3]^{-1}$ prepared by Forster previously (*22*). At this stage the reaction mixture was inactive for methyl acetate production. When only 40 psi (0.27 MPa) of CO was pressured onto the reaction solution at this stage, Curve B reappeared and the methyl acetate production continued. The spectrum of the high-pressure, 600 psi (4.14 MPa), active system at high methanol conversion is shown in Fig. 12. The coordination chemistry and mechanistic implications of these observations will be detailed in subsequent publications.

The above experiments serve to demonstrate three important capabilities of this spectroscopic method: (1) autogeneous analyses in strongly absorbing solvents; (2) facile condition adjustment to stabilize various catalytic intermediates relative to one another; and (3) simultaneous observation of various intermediates and rate of product formation to enable the identification of active and inactive species.

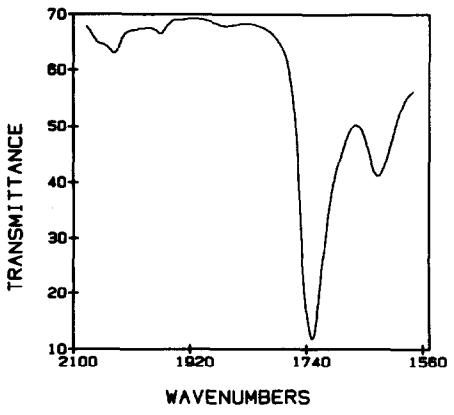

FIG. 12. Carbonylation of pure methanol at 150°C and 600 psi using a $RhCl_3 \cdot 3H_2O$—CH_3I catalyst.

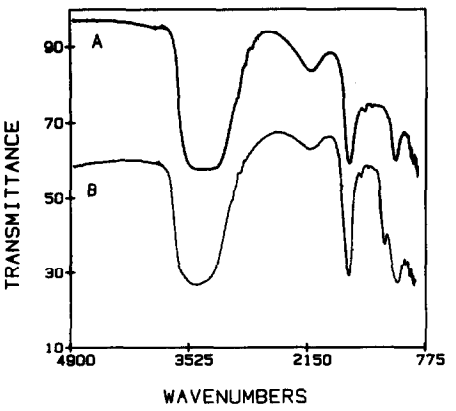

FIG. 13. Infrared spectra of H-ZSM5 synthesis in aqueous solution using procedure of Derouane and coworkers (*23*). Curve A measured after 2.5 h at 32°C. Curve B was taken after 22 h at 130°C. Five hundred scans were averaged using a resolution of 4 cm^{-1}.

IN SITU STUDY OF ZEOLITE CATALYST SYNTHESIS

An example of the synthesis of the zeolite catalyst, H-ZSM5 is shown in Fig. 13 to demonstrate two capabilities of CIR as an *in situ* spectroscopic method: (1) the method permits the examination of aqueous reaction solutions under autogeneous conditions and (2) the solids contained in the reactor do not interfere with the analysis of the liquid components of the mixture. These studies have been carried out while the reaction mixture was either stirred, or unstirred as is commonly the case in zeolite synthesis. The scientific information relating to zeolite synthesis which we have obtained using this technique is summarized as follows: (1) The chemical transitions in the template were easily followed; (2) the rate of disappearance of dissolved starting materials were easily measured; and (3) some information on gel formation, its transformations and disappearance could be observed.

The two spectra recorded in Fig. 13 show an early time (2.5 h) spectrum in Curve A and a spectrum measured after 22 h in Curve B for a H-ZSM5 synthesis using the procedure of Derouane and co-workers (*23*). An expansion of the 1450-cm^{-1} region

of the spectra permitted an observation of the compositional changes in the tetrapropylammonium bromide template used in the synthesis as a function of time. The 1100-cm^{-1} region was used to monitor the formation and collapse of the gel component. The CIR method does not observe the crystalline components of the reaction mixture while suspended in the aqueous media; however, high-quality spectra of crystalline zeolites were obtained when powdered samples were packed in the reactor in Fig. 2.

This technique has been used to examine the synthesis of ALPO-5 (*24*), and a high-Si/Al silicalite. A limitation which was observed in these studies, was the inability to study strongly basic solutions since they resulted in corrosion of the CIR crystals and loss of the IR signal.

APPLICATION TO OTHER SYSTEMS

Several other systems were studied by the CIR method and have provided mechanistic and synthetic data relating to catalytic research. As an example of organometallic reactions, the mechanism of metal hydride transfer was examined by the stoichiometric reaction of $IrH(CO)(PR_3)_3$ complexes with benzyl halides. Metal carbonyl displacement reactions were also studied in the reactions of Group VI hexacarbonyls and lithium amine chelates. Oxidation catalysis was readily examined in acetic acid solution for the cobalt-catalyzed oxidation of *tert*-butyltoluene. Extensive data have been obtained for syngas reactions in both methanol- and benzyl alcohol-catalyzed homologations catalyzed by both ligand-modified and unmodified cobalt systems.

The potential application of this type of embedded CIR crystal to *in situ* heterogeneous catalysis studies is illustrated by the infrared spectra of solid samples of a 1000/1 Si/Al H-ZSM5 zeolite in Curve A, and silica gel in Curve B. These spectra were measured after their powdered samples were packed into the low-volume CIR reactor shown in Fig. 2. The same type of measurement afforded typical rhodium carbonyl bands when alumina-supported rhodium was heated with synthesis gas.

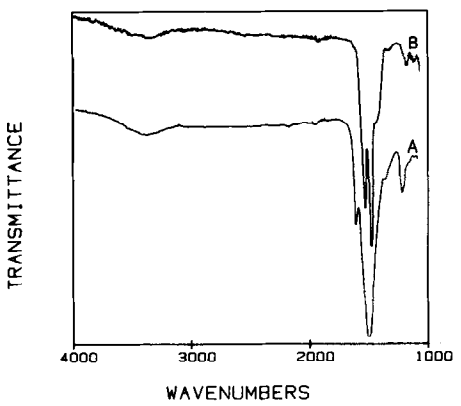

FIG. 14. Infrared spectra of solids packed into the cell shown in Fig. 2 using 2000 scans at a spectral resolution of 4 cm^{-1}. Curve B is a spectrum of silica gel and Curve A is a sample of a 1.000/1 Si/Al atom ratio of H-ZSM5.

DISCUSSION

The data above illustrate the unique capabilities of embedded cylindrical internal reflectance elements in high-pressure reactors for the study of catalytic reactions under autogeneous conditions. Although the method appears to be superior to any other *in situ* methods for the study of homogeneous-phase reactions, the technique inherently requires the analysis by a sensitive Fourier-transform infrared spectrometer. Exceptional sensitivity is required due to the low through-put of energy after passing through the 3-in. cylindrical internal reflectance crystal. In order to take full advantage of this short pathlength method of analysis, the spectrometer must have excellent spectral subtraction capabilities. We have observed problems in a few cases where catalytic intermediates could not be observed due to the very low applied total catalyst concentration. This is a consequence of the fact that CIR is a low-pathlength method. The problem may be overcome by the application of more sensi-

tive detectors such as MCT-A detectors which are commercially available.

Another disadvantage of the method is the fact that a range of crystals must be utilized for different types of analysis due to the corrosion of the polished crystal surface by some reaction solutions. When this happens, all infrared information is lost. This problem is not nearly as serious in transmission types of experiments. As an example, our studies showed that both zinc selenide and pure germanium optics were corroded by the aggressive cobalt iodide and cobalt carbonyl solutions. However, pure silicon and zinc sulfide worked exceptionally well for these studies. Only silicon worked well for the rhodium iodide catalyst in the Monsanto acetic acid system. Zinc sulfide has superior base erosion properties.

Special attention to safe operation of the equipment described here is required in both the design of the reactors and the operation of the experiment. Our method described in the experimental section used a low volume autoclave located in a separate compartment of the IR spectrometer continuously flushed with a high volume of nitrogen. Totally remote facilities using extended collimated infrared beams is another approach when an inert surrounding is not practical or when high reactor volumes or exceptionally high pressures are to be examined. We have no information on the use of the method above 2000 psi where the initial static tests were performed. Most of the data reported here were recorded in the league of 1200 psi. A low-volume, 5-ml reactor has been fabricated and is currently being tested. This reactor is designed for general catalytic experiments which may be run outside of specially barricaded cells at high pressures.

EXPERIMENTAL

Reactors. The reactors used in these studies were all fabricated from 316 stainless steel by Mr. Jack Ferraro of the Chemical Engineering and Chemistry Departments of Worcester Polytechnic Institute. The optical stage for the cylindrical internal reflectance experiments was obtained from Barnes Analytical, Stamford, Connecticut and is commercially available as part of their CIRCLE accessory for cylindrical internal reflectance. The internal reflection crystals, ZnSe, ZnS, Ge, and Si were also obtained from them. The direct-drive batch reactor utilized a design which is shown in Fig. 5. The reactor used a solid-Teflon insert, part D, in the figure to reduce the internal volume of the reactor. The reactor in this configuration had an internal free volume of 45 ml when empty while equipped with the crystal. This Teflon part is removable for the study of reactions requiring a large internal volume. This configuration was employed in the present studies out of safety considerations. The reactors were equipped with either cartridge heaters in the case of the configurations shown in Figs. 2 and 3; the direct-stirred reactor shown in Fig. 4 used band heaters secured to the outside skin and was controlled by a thermocouple located in a well in the wall of the reactor. In all reactors the temperature was constantly monitored by a thermocouple located inside the reactor in contact with the reacting solution.

Spectrometer. The spectrometer used in these studies was a Nicolet 60SX Fourier-transform infrared instrument equipped with an MCT-B detector. The infrared spectra shown in the figures were measured at a spectral resolution of 4 cm^{-1} by averaging 500 scans unless otherwise mentioned in the figure caption. No smoothing was applied to any of the displayed spectra. Background studies for each cylindrical internal reflectance experiment were taken in an empty cell at the reaction temperature employed by the subsequent catalysis experiment. These spectra were stored for future use using the computer facilities in the instrument. Spectral subtraction and deconvolution routines used those supplied by Nicolet. The calibration of the products to be analyzed by the infrared method were

carried out using a wide range of standard substance concentrations in the solvent pertinent to the specific experiments. The spectral resolution utilized was generally 4 cm^{-1} and the reported spectra generally used 500 averaged scans unless otherwise stated in each figure caption.

Catalytic studies. All catalytic reactions employed a sample chamber which was flushed constantly with a fast flow of nitrogen. In all cases the reactor contents were loaded inside of an inert atmosphere glove box under a nitrogen atmosphere and sealed before mounting in the reactor chamber. Background solvent spectra were recorded by separate experiments taken at the temperature used in the catalytic experiment under nitrogen pressure. The reactors were always pressure tested with nitrogen at near operating pressures before the experiment was continued. In most cases the reacting gases were pressurized into the reactor at ambient temperature followed by rapidly heating to reaction temperature. Spectra were then measured at various times along the reaction profile using 300 to 3000 scans at a line resolution of 0.5 to 4.0 wavenumbers depending on the requirements of the experiment. At the end of each catalytic experiment the contents of the reactor were determined to obtain a full slate of the final solution composition by gas chromatographic analysis using internal standards added at the end of the reaction. Appropriate response factors were determined and utilized in these analyses.

Materials. Chemicals used in the catalytic studies were obtained from commercial sources. Except for degassing in certain experiments the solvents were used directly without further purification.

ACKNOWLEDGMENTS

The authors are grateful for the close working relationship with Mr. Don Sting of Barnes Analytical-Spectra Tech and for his many suggestions. The reactors were carefully crafted by Mr. Jack Ferraro who made many excellent suggestions with respect to their mechanical configurations. We are much indebted to the National Science Foundation (Grant No. CPE-8218110) for support of part of this work which required our search for a better technique for the *in situ* study of catalytic reactions for low-pressure cobalt-catalyzed carbonylations.

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