Design and Use of a High-Pressure Stirred IR Cell for Operando Studies in Homogeneous Catalysis

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The design and operation of a new kind of high pressure/high temperature stirred IR cell is described. The cell is a stand-alone autoclave made of Hastelloy and effective stirring and gas diffusion are provided by a magnetically driven Teflon shaft. The length of the optical path can be regulated without the need of calibrated spacers and the problem of the sealing of the windows to the cell body has been solved by employing FEP (fluorinated ethylene propylene) encapsulated Viton O-rings, which, upon adapting to the cell when warmed, provide an excellent seal that is also tolerant of all standard solvents. The use of this kind of O-rings allows taking advantage of the chemical resistance of Teflon without needing to mechanically stress the fragile windows as it would be required if bulk Teflon O-rings were employed.

1. Introduction

Operando techniques have always been instrumental in understanding the mechanism of chemical reactions, but the recording of good quality IR spectra at high temperatures and pressures, necessary to investigate the mechanism of homogeneously catalyzed carbonylation and hydroformylation reactions, poses some specific problems that are not easily solved. It is not the purpose of this paper to review all the literature in the field and the reader is referred to previous reviews for a more complete discussion.[1–5] However, we will briefly evidence some features of previously reported systems to clarify which are the weak points of each configuration and allow a discussion of the solutions we propose for each of them. Note that many papers are devoted to the study of heterogeneous catalysts.[6,7] These studies pose different problems with respects to those encountered in the study of homogeneous reactions and the corresponding experimental set-ups will not be discussed here.

The experimental configurations that have been employed to record IR spectra under high temperature and high pressure conditions can be roughly divided in two groups: those in which a "traditional" autoclave is connected by metal tubing to an external heated cell able to withstand the pressure and those in which the autoclave itself is built in a way that allows the IR beam to pass directly through it.

Although excellent results have been obtained in some cases,[8–11] the disadvantage of the former class is that the recirculation of the solution can give rise to pressure drops or bubble formation, resulting in a recorded spectrum that is not truly representative of the conditions inside the autoclave. Even a fast consumption of a reacting gas (CO and/or H_2) after the solution has left the stirred autoclave can cause the same problem. A recent improvement of this type of system involves the use of a micro gear pump to speed-up the transfer of the solution from the autoclave to the IR cell, thus shortening the delay time.[9,12]

Performing the measurement directly inside the autoclave solves the aforementioned problems, but a traditional autoclave is clearly too wide to allow the transmission of an IR beam. Moser introduced a cylindrical internal reflection crystal (CIR) into a standard Parr Mini Reactor.[13] This principle has evolved in the development of commercially available flexible inlet probes that can be fitted to an existing autoclave and are connected to the IR spectrophotometer by an optical fibers cable. The physical principle on which these systems operate is that of ATR and the limit is the small penetration depth of the signal into the solution resulting in a low sensitivity and a relatively bad signal-to-noise ratio.[4,11] Additionally, the material of the probe material can also be a concern. The two materials employed in the commercially available probes are silicon and diamond. However, silicon may be attacked by some chemicals and diamond presents a strong absorbance in the 2700–1800 cm^{-1} range,[14] making it unsuitable for the investigation of metal-carbonyl or metal-hydride complexes.

The best solution in terms of getting the highest quality IR spectra, still fully representative of the real situation during the reaction, is to build a special autoclave having windows at the proper distance to record an IR spectrum in the transmission mode. The design and operation of a few such autoclaves has been reported in the literature.[4,8,15,16] Each design has its advantages and disadvantages, but a common problem is the

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material used for the O-rings that guarantee the sealing of the windows to the autoclave.

Several years ago, we designed a high pressure/high temperature stirred IR cell that allows the continuous recording of IR spectra while the reaction is performed. The IR cell was employed to collect data that have been published in several works on rhodium- and ruthenium-catalyzed reductive carbonylation reactions of nitroarenes by CO to give carbamates,[17–20] allylic amines,[21] oxazines and pyrroles,[22] but the design of the IR cell has never been described. Upon using it, we optimized the operational procedure and describe here both the cell design and some tricks we found to operate it at the best. Without wishing to say that we have solved all problems, some
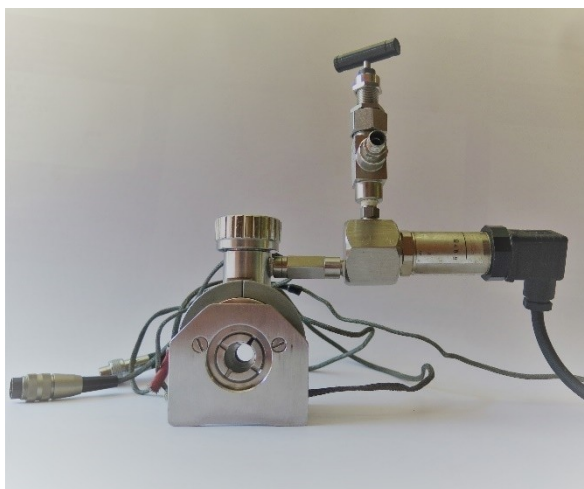
of the solutions we found may be of interest even to those operating different types of cells.

2. Results and Discussion

A front and a side view of our IR cell are shown in Figures 1 and 2. A schematic drawing of a section of the cell is shown in Figure 3.

The body of the cell is made of Hastelloy C-4, an alloy with exceptional resistance to a range of aggressive chemicals.[23,24] Gases are charged through a side port placed in the upper part of the cell, which is also used to fit the electronic pressure gauge. The cell is heated by a heating mantle controlled by an external control unit, also connected to a thermocouple. Two stainless steel plates maintain the cylindrical cell in an upright position when not in use and fit the corresponding slits in the cell support (see later, Figures 7 and 8), keeping the cell in position inside the IR compartment.

The most peculiar feature of our cell is represented by the stirring shaft. This is schematically shown in Figure 3 and a side and a bottom pictures are shown in Figure 4. The shaft fits into the cylindrical cavity of the cell. The cavity terminates in a round flat surface through which three holes (Figures 3 and 5) provide a connection to the lower part of the cell, where the actual IR measurement is made.

Figure 1. Front view of the cell. On the right, it is possible to see the valve for the admission of gases and the electronic pressure gauge.
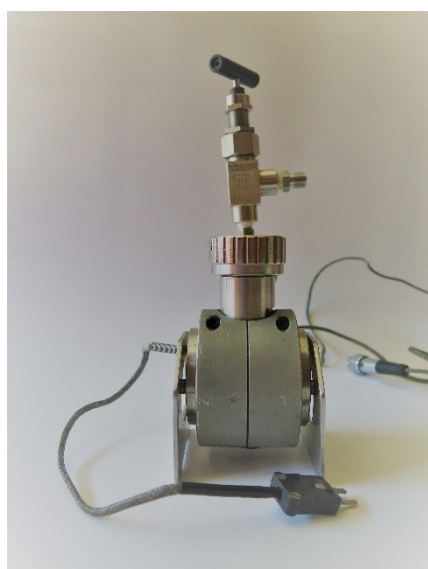

Figure 2. Side view of the cell. The cylindrical grey part is the heating mantle. A thermocouple is inserted in the autoclave body and protrudes from the left side in the picture. The upper cap allows access to the cell when the windows are mounted, for the introduction of solutions and the cleaning of the cell.
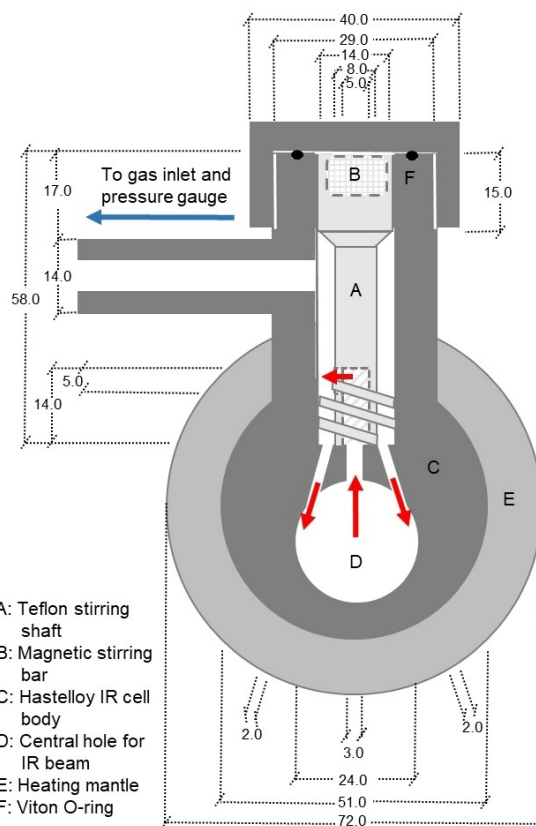

Figure 3. Simplified vertical section of the cell. Screw threads are not shown. Quotes are in mm. The red arrows indicate the direction of the liquid flow when the cell is stirred.
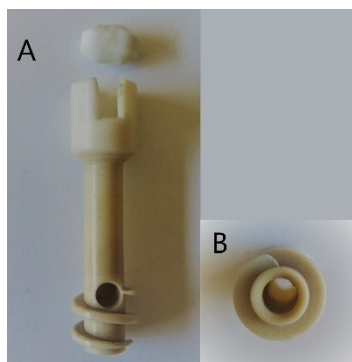
A: Teflon stirring shaft
B: Magnetic stirring bar
C: Hastelloy IR cell body
D: Central hole for IR beam
E: Heating mantle
F: Viton O-ring

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Figure 4. Side (A) and bottom (B) view of the Teflon stirring shaft. The magnetic stirring bar visible in A is placed inside the corresponding cavity on the upper part of the shaft. A coaxial hole is drilled in the lower part of the shaft to allow the solution to be sucked upward through it and be dispersed through the side hole.

Figure 6. A: Cell without windows, window holder and extraction tool. B: A window holder with window and Viton O-ring in place.

Figure 5. Upper view of the opened cell, showing the three holes that connect the stirred part of the cell with that where the IR beam passes through and the side port connecting the cell body to the gas valve and pressure gauge. A light was inserted in the lower compartment to improve the contrast in the picture.

When stirring is turned on, the helicoidal part of the shaft pushes the solution downward into the cell part where the IR beam passes through (see the red arrows in Figure 3). At the same time, the solution is sucked from the lower compartment into the upper one through the central hole and the coaxial hole in the shaft. This results not only in a mixing of the solution, but also in a very efficient dissolution of the reacting gas.

Coming to the lower part of the cell, this features a cylindrical cavity perpendicular to the upper one and terminating on both sides with a threaded part that matches the two window holders. The thread has a 1 mm pitch. The cavity and a window holder are shown in Figure 6A. Also shown in this figure is the custom-made extraction tool (on the left) employed to tighten the window holders, fitting two of the four perpendicular slits cut into the window holder itself (The slits are better visible in Figure 1). Figure 6B shows the window holder with a window and a Viton O-ring in place.

Two short videos showing the best procedure to assemble the cell are present in the Supporting Information. Here, we focus on a few general points.

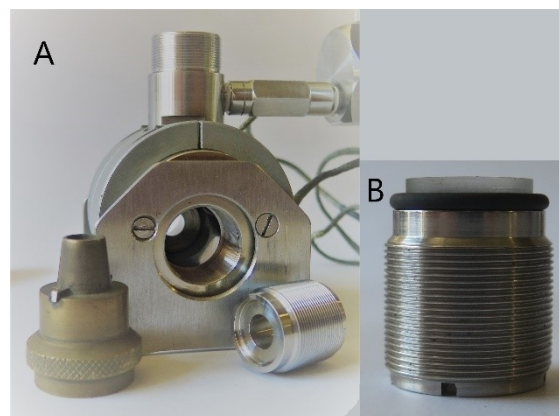The cell has no spacer to control the optical path length. Though spacers are often employed in this kind of cells, they can cause the formation of stagnant areas in the cell chamber or anyway hinder an even mixing of all the solution. The windows are kept in their place by the internal pressure under operating conditions. This setting requires a calibration of the optical path. This was made just once by tightening the window holders to the end position and measuring an IR spectrum of the empty cell. Since the method is known, the reader is referred to a textbook for a complete description.[25] In short recording an IR spectrum of an empty cell causes the formation of regularly spaced interference fringes, whose number is directly proportional to the width of the empty space. The optical path length is given by $\frac{1}{2}$ of the quotient between the number of fringes observed in a chosen frequency interval and the difference between the wavenumbers of the extremes of the interval. By this measurement, we determined that with the employed windows (IRTRAN-1 (MgF2) $\phi = 20$ mm, $h = 6$ mm), the minimum spacing is 0.2 mm. However, working at this path length value was found to be unpractical because under strong stirring conditions, some gas bubbles tend to remain entrapped between the two windows and lead to problems in the recording of the spectra. Thus, we routinely assemble the cell to the minimum spacing and then untighten one of the two window holders by applying a 90° counterclockwise rotation (corresponding to a 0.25 mm movement of the front window), thus operating at a 0.45 mm optical length spacing. It is worth noting that Kamer and van Leeuwen independently reported that they made most of the measurement with their IR cell working at a 0.4 mm spacing.[4] Thus, an optical path length of this order of magnitude appears to be ideal in the view of different groups. Note that further increasing the path length can result, depending on the solvent employed, in an excessive light absorption and the impossibility to record the IR spectrum or in a low quality of the same.

A key point for the obtaining of good results is the material of the O-rings sealing the windows. Teflon has been used for the CIR reactor mentioned in the introduction and for some other cells based on the ATR technique, but even in these cases its use can be problematic and specially designed gaskets may be needed to reduce the risk of breaking the brittle ATR

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crystals.[26] We are not aware of any report in which very hard Teflon O-rings have been successfully employed to seal high pressure IR cells working in the transmission mode. In general, most authors appear to employ Viton O-rings for many measurements and more resistant, and much more expensive, Kalrez O-rings in more critical cases,[1,3,4,8] although a more complex set of Viton and silicon O-rings has also been mentioned.[27] However, whereas these materials are quite resistant to low polarity or protic (e.g., methanol) solvents, they are easily attacked by medium-to-high polarity non-protic solvents. Our first attempts to use this IR cell were in the field of the carbonylation reaction of nitrobenzene to methyl phenylcarbamate,[17,18] a reaction that required heating at 160 °C a 8:3 THF/methanol solvent mixture also containing some nitrobenzene and, in some cases, pyridine. Much to our disappointment, Viton O-rings started to dissolve well before the final temperature was reached causing the solution to become black and all infrared radiation to be absorbed before the cell eventually started to leak. Kalrez O-rings did not perform any better under the same conditions. As a matter of facts, we are not aware of any high pressure-high temperature study employing a transmission cell and such aggressive solvents, although plenty of room exists for investigating catalytic reactions that employ them.

In search for an alternative that may be suitable with any solvent, we resorted to the use of FEP encapsulated O-rings. FEP (fluorinated ethylene propylene) is a copolymer of hexa-fluoropropylene and tetrafluoroethylene. It was invented at DuPont and is sold under the brand name Teflon FEP. Other brand names are Neoflon FEP from Daikin and Dyneon FEP from Dyneon/3M. FEP has a higher flexibility than Teflon, albeit a lower maximum operating temperature (204–205 °C according to different producers), which is anyway high enough for most chemical purposes. It also has basically the same solvent resistant properties of Teflon and can be thus employed with any solvent, with the only exception of fluorinated ones.

FEP encapsulated O-rings are commercially available with an inner Viton or silicone O-ring (we employed the former) surrounded by a FEP transparent layer. They are more expensive than Viton O-rings, but considerably cheaper than Kalrez ones. Though still relatively rigid at room temperature, FEP has a glass transition temperature of 80 °C,[28] over which it becomes flexible enough to be adapted to the windows. Briefly warming the O-ring on a heating gun (setting the air temperature to 100 °C) is enough to allow for this. The first of the videos mentioned before shows this procedure.

Once the O-rings have been adapted to the windows, the cell can be assembled (see the second video). At this stage, the cell can be loaded with a solution and pressurized, but the sealing is still not perfectly tight and a small leak can be observed. However, if the cell is immediately heated over 80 °C, the inner pressure deforms the O-rings resulting in a flattening of the outer side and a perfect adherence to the window holder and cell walls. At this stage, not only is any leakage stopped, but the sealing remains excellent even once the cell is cooled down to room temperature. The cell can thus be employed for a series of consecutive experiments, even over several days,

without any problems. When the windows are dismounted, the "flattened" O-rings can still be employed again, repeating the cell "heating" stage, but upon repeated use the FEP layer tends to crack and expose the internal Viton core, so that the integrity of the outer layer should be carefully checked before using it for a further series of experiments. Note that the upper cap of the cell is also sealed by an O-ring, but this O-ring is outside the solution and Viton can be used without problems even in the case of aggressive solvents, although it may be necessary to change it after a few reactions.

In our studies, we employed the cell up to 170 °C and 80 bar with no problem ever, but the cell was also tested at RT up to 140 bar (with water as the liquid phase and air as the compressed gas). However, note that because of the material the cell is built of and the width of its walls, the "metal" part of the cell is expected to withstand several hundred bars. It is the windows to be the weak point and their resistance depends on the material they are made of and their dimensions. Thus, technical data from the windows seller should always be consulted.

We are not aware of any previous use of FEP encapsulated O-rings in the field of high pressure spectroscopic studies of chemical reactions, but our results suggest that their use, with the expedient described above, may represent a major improvement even for other cells actually employing different types of O-rings or gaskets.

Once assembled, the cell can be loaded with the reagents (all in solution) from the upper port while being flushed with dinitrogen. The central shaft must be removed at this stage. A total volume of 2 mL was found to be ideal for an effective stirring and gas diffusion. The shaft is then introduced and the cell closed and pressurized with the desired gas (we always employed CO, but other gases are compatible with the cell).

To host the cell in the infrared spectrophotometer, a support was designed having a screw and two protruding pivots that fits the holes present in the instrument compartment, so that no alignment is necessary once the cell is placed in the fixed support. A front and an upper view of the support are shown in Figure 7. The support can be cooled by a flow of water circulating in a metallic hose weld to the support. Cooling of the support is important when high cell temperatures are reached, to avoid heating the spectrophotometer.
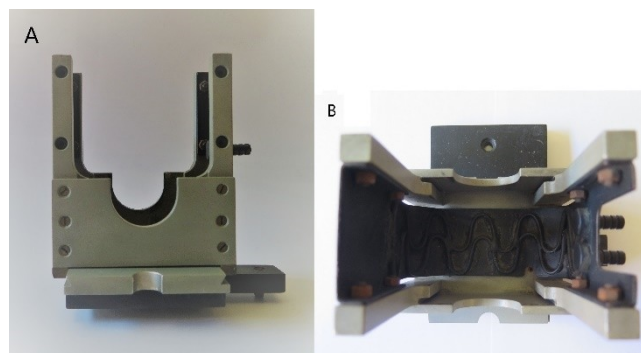

Figure 7. Front (A) and upper (B) vies of the cell support.

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The set-up is completed by an additional support that joins the cell support to an upside-down magnetic stirrer. The complete set-up is shown (outside the IR spectrophotometer) in Figure 8.

It should be mentioned that a standard magnetite magnetic stirring bar was employed when the cell was built, which requires a relatively powerful stirrer to guarantee an efficient rotation of the shaft. However, nowadays Teflon-coated magnetic stirring bars made of rare-earth magnetic materials such as Nd—Fe—B are commercially available, that may allow the use of a smaller stirrer or even a contactless coupling of the internal with an external rotating rare-earth magnet, thus eliminating a source of vibrations on the IR instrument.

As far as operating suggestions are concerned, it is usually not stressed enough in the literature that the baseline absorptions depend on the temperature. To get a good baseline subtraction, it is essential to record a series of spectra of the solvent under pressure at all the temperatures at which the reaction is planned to be investigated (at the very least, the spectrum of the solution at room temperature before the reaction is started and after complete cooling at the end of the same should be recorded to allow a better comparison with the spectra of known compounds). Since the background may change over several days, it is convenient to record the solvent spectra series as background-referenced spectra, do the same for the reaction spectra and finally subtract the former from the latter. To allow this, the cell should be dried by extensive flushing with compressed air and dinitrogen after the solvent series is recorded, but the window holders and the windows should be let in their position until the full series of experiments is completed. Washing with a solvent added by a syringe with a needle narrow enough to enter the lower compartment without scratching the windows or repeatedly washing the lower compartment by taking advantage of the shaft rotation are additionally needed when several experiments must be performed.

When a solvent mixture is employed, even slight changes in the solvent mixture can cause a sensible change in the baseline.

Figure 8. Complete set-up (outside the IR spectrophotometer).

Thus, when this is the case, it is mandatory to prepare enough of a stock solution of the mixed solvent to perform the collection of the "solvent" spectra series and be employed for all of the planned experiments.

When recording the solvent spectra series, it is a matter of choice to employ the actual gas that will be used in the following experiments or an inert gas, e.g. N_2, to pressurize the system. When CO is part of the reacting gas, it should be considered that although this molecule has a low dielectric moment and its IR absorption is barely visible when the IR spectrum of a solution under 1 bar of CO is recorded, an intense absorption is observed under a pressure of 30 bar or more. If the solvent reference series is recorded under CO pressure, the baseline will be initially flat in the region where the dissolved gas absorb (around 2143 cm^{-1}, depending on the solvent) but a negative peak will be detected as the reaction proceed.

The described IR cell has been employed both to identify the carbonyl complexes present under actual reaction conditions and to study the kinetics of a nitrobenzene reduction, by following the disappearance of the absorption of the substrate. Representative spectra have already been published in some of the previously cited papers in which we made use of this cell.[19,21–22]

3. Conclusion

In this paper we have described a high pressure/high temperature autoclave that can be used for operando spectroscopic studies. It should be noted that although the cell was designed to record infrared spectra, use of quartz windows may render it suitable even for UV-Vis studies without any other modification. We used MgF$_2$ windows because of the high mechanical resistance and low solubility of this material. The fact that MgF$_2$ is opaque at wavenumbers lower than 1100 cm^{-1} was not a problem to us, but if recording spectra at lower wavenumbers is desired, other window materials can be employed.

The low operating liquid volume (around 2 mL) can be an advantage, but requires care in the loading procedure to avoid any contamination of the reagents. The fact that the gas phase volume is also limited constitutes a safety aspect, but may represent a problem if a catalytic reaction is performed at a relatively low pressure. In this case, the pressure drop during the reaction may be significant. Connection of the cell to an external source of gas can be a solution, but safety would become an issue.

A limit of our cell is that no addition of reagents during the reaction is possible. This is a feature that is usually available only on larger autoclaves. Modification of our cell to allow it is in theory possible, but the small operating volume would make the loading of additional liquids not easy to manage.

We think that one of the points discussed in this paper that may raise the widest interest among those working with operando techniques is the way we employed FEP encapsulated O-rings. A simple warming of the latter allows using them in conjunction with fragile materials that would not resist the compression required by a Teflon O-ring or gasket to give a

gastight sealing, still without losing the advantages associated to the chemical inertness of a perfluorinated material.

Conflict of Interest

The authors declare no conflict of interest.

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