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High-Pressure High-Temperature Transparent Fixed-Bed Reactor for Operando Gas-Liquid Reaction Follow-up

Research Article

Authors:

Marisa De Sousa Duarte, PhD

Matthieu Rolland*, PhD

Corinne Sagnard,

Didier Suire,

Frederic Flacher,

Olivier Delpoux, PhD

Charles P. Lienemann, PhD

Affiliation :

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France

*Corresponding author: matthieu.rolland@ifpen.fr

Abstract

A 3 MPa, 350 °C fixed bed reactor has been designed to follow-up gas-liquid-solid reactions on a millimetric size heterogeneous catalyst with Raman spectroscopy. The transparent reactor is a quartz cylinder enclosed in a joule effect heated stainless steel tube. A methodology to determine how to focus the microscope for liquid and solid phase characterization is presented. The set-up has been validated by performing diesel hydrodesulphurisation on a CoMo/Alumina extrudate catalyst with a conversion very close to expected values along with the acquisition of Raman spectra of the solid catalyst showing an evolution of the catalyst phase during sulfidation.

Keywords: Diesel hydrodesulphurization, Gas-Liquid reactions, *Operando* Raman spectroscopy, Reactors Fixed bed

1. Introduction

Most of the knowledge acquired on catalysts active phase has been gained using characterization of samples before and after the reaction through the application of *ex-situ* techniques, specifically in very different chemical environment from that of the operating catalyst in a reactor. To link catalysts structure/composition with their activity and selectivity, it is very interesting to couple a spectroscopic characterization on the solid phase with an analysis of the effluents at the reactor exit which is called "*operando*" [1–4]. Electron based spectroscopies, XPS (X-ray Photoelectron Spectroscopy) and TEM (Transmission Electron Microscopy) are inherently limited in pressure (few mbar) [5–7]. NMR (Nuclear Magnetic Resonance) probes are limited in temperature with a current

limit near 267 °C [8]. IR (Infrared spectroscopy) experiments, despite its early *operando* application [9–11], make use of probe molecules, and therefore are conducted at temperatures compatible with adsorption of the probe molecules to the catalyst surface. Other spectroscopic techniques, such as Raman, EXAFS (Extended X-ray Absorption Fine Structure) and UV-visible absorption, are more flexible in terms of reactor operating conditions, the limiting point being the reactor design. For instance, Raman spectroscopy has been carried out up to 500 °C at atmospheric pressure [12–14] and 24 MPa at ambient temperature [15], and EXAFS measurements up to simultaneously 600 °C and 5 MPa [16–19].

So far, none of the *operando* reactors has been designed to operate gas-liquid-solid reactions under high pressure and temperature. The first *operando* studies focused more on the good quality of the spectroscopy data than on the chemical engineering aspects. Due to inhomogeneities in catalyst temperature and mass transfer limitations, the cells were assessed as not adequate for the characterization of catalysts in reactive environments [1,14]. Moreover, the majority of these studies were performed on powder catalysts whereas industrial processes are carried out with extrudates shaped catalysts. An *operando* systems design for millimetric heterogeneous catalysts would also be of great interest. Typical industrial catalysts are poly-lobed extrudates with diameter in the range 1.2 to 1.6 mm and length in the range 2-6 mm.

This paper covers the design of a high pressure (3 MPa), high temperature (350 °C) cylindrical transparent fixed bed reactor, suitable for *operando* Raman spectroscopy investigation on extrudate catalyst pellets as well as the development of a Raman-based characterization method to acquire real-time spectra in various spots along the reactor at different catalyst lifetimes. The set-up has been validated on hydrodesulphurization (HDS) of Diesel on a CoMo/alumina catalyst. This reaction has been chosen as a challenging validation case: it aims at removing almost all the sulfur from transport fuel so as to prevent acid rains. The residual sulfur level of around 10 wt. ppm is very low which requires a near perfect hydrodynamic [20]. The reaction being exothermic and sensible to temperature, the reactor design must ensure that catalyst temperature is within a few degrees of the specified temperature.

2. Reactor design

2.1 Constraints

The main requirements that have to be considered in the design of a cell desirable for spectroscopic Raman reaction *operando* follow-up are: transparency, mechanical strength to support the desired operating conditions (350 °C and 3 MPa), absence of leaks for safety and mass balance reasons, plug flow without mass transfer limitations and with an isothermal temperature profile along the reactor. The reactor should be filled with poly-lobed catalyst extrudates as described in the introduction. In order to be used with our current Raman spectrometer, the total weight on the microscope moving stage must be less than 1 kg. The objective lens should be no more than 1cm away from the catalyst surface, and the set-up width should be less than 22 cm to fit inside the Raman device.

2.2 Design

2.2.1 Transparent millimetric reactor

Studies performed by Kallinikos and Papayannakos [21] have shown that a tubular reactor 2 m long and with a 2 mm inner diameter, coiled in an ascending spiral shape, gave excellent diesel HDS results with catalysts extrudates. An unpublished work gave hints that a 2 mm internal diameter reactor allows sufficient heat and mass transfer to perform HDS of Diesel even for reactor as short as 23 cm. Here, a horizontal reactor was chosen: being parallel to the moving stage facilitates the focus procedure for several axial positions.

Glass, quartz or sapphire are suitable materials for Raman cells construction because of their optical transparency in the visible range. Nevertheless, glass is not a suitable option because of its low mechanical resistance at 350 °C. Additionally, as reactants may foul the reactor surface, it will be a bonus if the reactor could be disposable after each catalytic test, which for cost reasons precludes the use of sapphire. It has been decided to use a reactor made of quartz.

Material resistance calculations were performed to assess how thick the reactor should be. Reactor failure can occur for two reasons: first pressure inside the reactor resulting in too high tensile stresses and sudden material failure, and second, stress concentration near a defect resulting in crack propagation from the defect, which in glasses also means failure. In a pressurized cylinder, stresses can be evaluated using classical textbook formulas [22]. At 3 MPa, the risk of failure comes mostly from crack propagation from a defect. Quartz mechanical properties are readily available at ambient temperature but not at 350 °C. We considered that quartz at 350 °C would not soften and used ambient temperature properties with a significant safety factor. A 6 mm external diameter is thick enough to ensure a safety factor of 6 as long as no defects larger than 0.1 mm are present, which can be checked visually. Thicker reactors do not increase the safety factor. This design yields a minimum 2 mm reactor thickness compatible with the Raman microscope focal length of 1 cm.

A cylindrical shape has been chosen for cost and availability reasons. A thicker tube with a polished flat surface has been considered, but as we will show in the “focus methodology” section, a curved surface can be handled. To conclude, we opted for a horizontal quartz made cylindrical reactor with dimensions: 2 mm inner diameter; 6 mm outer diameter; 23 cm length (to fit inside the Raman spectrometer).

2.2.2 Heating device

The chosen heating system consists in a stainless steel tube heated by Joule effect. This solution minimizes the weight of the set-up as well as distance to the microscope lense compared to the more classical design of oven blocks with openings for optical access [1,2,14,23,24]. The heating stainless steel tube is machined with a slit window for optical access (Figure 1). The stainless steel tube acts as support, heater and shield in case of quartz failure. Heating tube inner diameter was chosen 0.2 mm larger than the quartz diameter to ensure the quartz tube does not touch the heating tube accounting for tolerances in quartz rods. Thermal expansion is not an issue here as quartz expands less than stainless steel.

((Figure 1))

Heat is generated by circulation of a low voltage (2.1 V) high intensity alternative current (around 90 A) in the stainless tube. In order to help the design and achieve a near isothermal temperature profile in the catalytic zone (around 7 cm), numerical simulations have been performed to simulate the thermal and current fields using the *Comsol multiphysics* software. The simulations showed that the best temperature profile is achieved when the heat is mostly generated in the legs between the connectors and the stainless steel tube, which leads to long and narrow legs (Figure 2). With the optimized stainless steel tube geometry, the simulations indicate that the temperature in the quartz reactor center is practically constant over the reactor length (± 2 °C) and near constant in the catalyst even if the slit window induces a 2-3 °C cooling of the outer surface exposed to air compared to the reactor center. The slit window being longer than the catalyst bed length, this cooling has not effect on the axial temperature profile.

((Figure 2))

2.2.3 Complete design

The set-up design is presented in Figure 3 with all parts: tightness fittings, heating tube and power cables. Tightness around the reactor is achieved by using graphite/polyamide ferules compressed by steel nuts onto the reactor. A support plate holds all the parts together and onto the moving stage. It is made with PEEK (PolyEther Ether Ketone) that presents excellent temperature resistance, electrical insulation and is easily machined. The set-up is placed inside a custom made ventilated black box placed around the microscope head.

((Figure 3))

A pair of thermocouples is placed inside the reactor, at the beginning and end of the catalytic bed, with a double purpose: temperature measurement at both the catalytic bed ends and keeping the catalyst pellets in place. The inlet thermocouple is used for the temperature regulation. Thermal profiles depend greatly on the location of the insulation wool and on the air flow around the set-up, and can be readily tuned. In the final configuration, a temperature of 352 ± 2.5 °C is achieved on the 7 cm long catalytic bed zone. Such accuracy is highly sufficient for the planned *operando* studies. The remaining set-up parts are classical and not presented in this paper. This reactor withstood pressures up to 26 MPa during room temperature hydraulic experiments. The system was also tested under 350 °C and 6 MPa of nitrogen during 24 hours, without pressure losses. The test pressure was twice the operating pressure to comply with local regulations about pressurized equipment made with glass type materials.

2.2.4 Fluid flow pattern inside the reactor

Gas-liquid repartition in each section inside the reactor will have an impact on how the laser beam is refracted and focused. Hydrodynamic literature suggests a Taylor stratified flow pattern inside reactors of 2-4 mm inner diameter for both gas-liquid [25] and gas-liquid-solid [26] systems. In those conditions, the flow pattern is governed by capillary forces with little effect of the gravitational ones [27]. To confirm this, flow experiments were run at room temperature using hydrogen and n-heptane, which has almost the same surface tension and viscosity as a Diesel at

350 °C. Flow-rates were chosen to have the same volumetric flow-rates at reaction temperature and pressure. Additional observations were performed with Diesel at room temperature with similar results. The conclusion would be similar for all type of biomass-based and fossil feedstocks.

As expected, the experiments showed a Taylor flow type inside the reactor. With the chosen flow-rate, motion is very slow and hardly visible in most places: it takes 54 minutes for the liquid to cross the 7 cm catalytic bed. In any location, the flow can be of two types and does not change over time:

- i. wet catalyst particle and gas, named gas section, and sometimes a thin liquid layer at the reactor top (Figure 4a),
- ii. immersed catalyst particle with sometimes some gas bubbles, named liquid section (Figure 4b).

((Figure 4))

2.3 Raman acquisitions in a transparent cylindrical reactor

In *ex-situ* Raman experiments, the signal is acquired by focusing the laser beam on or inside the sample to be analyzed. In the transparent reactor, this is not as straightforward for three reasons. First, the reactor is cylindrical and will deform the beam. Second, the reactor may be filled with liquid, or gas and liquid. Third, catalyst pellets have a complex shape with lobes and they can be tilted and rotated as seen in the Figure 4. It is therefore impossible to know beforehand where to focus. A methodology to solve all three issues will be presented after some explanations.

Our cylindrical reactor presents a curvature in the transverse plane but not in the axial plane. The incoming beam, circular outside the reactor, will therefore deform differently in both directions when passing through the reactor (Figure 5). The resulting beam shape inside the reactor is an ellipsoid of varying shape and dimension when going downward. The Raman effect is proportional to beam specific intensity, defined as the laser power divided by the beam cross-section. The back scattered Raman photons, will mostly be generated in volumes where the beam cross section is minimal. The beam cross section present two minima, denoted as “focalization points” afterwards, located where the beam would focus if the reactor was flat, and if the reactor was a sphere of the same radius and thickness as the reactor (Figure 5). At these focalization points, the beam is a very narrow and elongated ellipse, appearing as a line. In other words, in the cylindrical reactor the focalization spots are lines. Line direction is perpendicular for both focalization points. When changing the moving stage vertical position, the focalization points will move through the reactor.

((Figure 5))

When a light beam encounters an optical interface, a small part of the incident light is reflected back to the optical camera. An optical interface is defined as a significant change of the refractive index. The reflected light from the laser is usually not visible except when the beam focuses at an interface. Very bright lines will be observed in the microscope when one of the focalization points meets an optical interface. In the gas section of the reactor, the liquid near the catalyst will form a thin film squeezed between the bubble and the wetted catalyst: the gas/liquid and liquid/solid interfaces cannot be distinguished. To summarize, in any section of the reactor, two optical interfaces are likely to be observed: 1) in liquid sections, quartz/liquid and liquid/solid and 2) in gas sections, quartz/gas and gas/wet solid. Combined with the two focalization lines due to reactor curvature, a vertical scan inside the reactor will give out four locations where the beam is focused on an interface and appears as a line. The four vertical locations where the beam focalize as a line are identified and named Z_1 to Z_4 , Z_4 being the deepest location, corresponding to an interface with the solid (Figure 6). The local flow pattern is deduced from the image contrast that is much lower when liquid fills the entire reactor.

((Figure 6))

Raman spectra have been acquired at various locations and presented properties of the spectra of quartz, liquid and catalyst. Quartz is visible in the Raman spectra recorded at Z_1 and Z_2 positions. Liquid Raman signature is visible in all locations mostly because of the fluorescent nature of the Diesel and did overwhelm the catalyst signal in most cases. The catalyst Raman spectrum is only visible in the ‘gas’ sections, being most intense at Z_4 . Neither intermediate locations between Z_3 and Z_4 , nor locations deeper than Z_4 improved the catalyst spectra quality.

To conclude this section, the focusing methodology has been developed and consists in:

- 1) Choosing an axial location in the reactor
- 2) Determining the vertical positions where the bright lines appear on the images, denoted Z_i ($i=1, 2, 3, 4$),
- 3) Acquiring spectra at Z_4 .
 - a. In ‘gas’ section, the spectra will contain liquid and catalyst signatures.
 - b. In ‘liquid’ section, the spectra will contain only liquid signature. To measure catalyst, it is necessary to change the axial location in the reactor and restart from step 1.

This methodology is a major advance to measure Raman spectra of a catalyst randomly positioned and oriented in a cylindrical reactor.

3. *Operando* Raman measurements at 350 °C and 3 MPa

3.1 Materials

Raman spectroscopy is performed using a Horiba Jobin Yvon Aramis microscope in backscattering configuration and an excitation line of 532 nm provided by a Nd-YAG laser, equipped with a dielectric filter and a grating with 1800 lines/nm, resulting in a spectral resolution of around 1 cm^{-1} . The laser power is 16 mW and the exposure time is set to 300 seconds for solid measurements. The final spectrum is the average of two acquisitions. The Raman spectrometer is equipped with a 3 axis moving stage where the reactor is placed on.

The sulfur concentration in the stripped effluent collected at the reactor exit is monitored by Wavelength Dispersive X-ray fluorescence (K α line) on a PANalytical Axios instrument equipped with a Cr anode and working at 3 kW. HDS catalyst is a commercial CoMo/Alumina catalyst (%Mo ~19-22%, %Co ~ 3-5%, S_{BET} ~ 200-260 m^2/g) shaped in 1.6 mm diameter quadrilobic extrudates.

3.2 Operating conditions

All the hydrodesulphurization experiments were carried out with a gasoil containing 0.64 wt. % S. Reaction conditions were: space time = 1.1 h^{-1} , temperature = 350 °C, pressure = 3 MPa and gas-to-liquid ratio = 240 Nm^3/m^3 .

Catalyst activation was carried out with a low fluorescent Diesel spiked with 1 wt. % DMDS, under 3 MPa and a temperature profile consisting of a ramp of 40 °C/h up to 350 °C, followed by a 18 h plateau at 350 °C.

3.3 HDS performance

Operation of the transparent reactor has been validated by performing HDS of the Diesel at 350 °C, 3 MPa during four weeks. Sulphur contents of 80-90 wt. ppm were measured, compared to 50 wt. ppm expected in those conditions with conventional reactors with the same catalyst, feedstock and operating conditions (conversion of 98.75 wt. % vs. 99.22 wt. %). The agreement is quite satisfactory with respect to the studies we plan to perform. HDS performance might be improved by slightly tilting the reactor; however, it would make the peek support machining more complex and the focus procedure a bit longer. The actual configuration is representative enough for an *operando* set-up designed to acquire new information on HDS reactions.

3.4 Raman spectra

First of all, the Raman spectra of the liquid phase exhibit fluorescence and could not be used to give insight about conversion degree.

Regarding the catalysts, Raman spectra of CoMo/Al₂O₃ in its oxide state (recorded at 25 °C, 3MPa H₂ in the reactor), and after sulfidation during HDS operation (350 °C, 3 MPa H₂ and in presence of flowing Diesel) are presented in Figure 7. First we can notice in all the spectra, the characteristic rotational lines of H₂ in gas phase at 355, 585, 815, 1035 and 1555 cm^{-1} [28]. The oxide state catalyst spectrum (pink spectrum) is composed of a large band centered at 950 cm^{-1} corresponding to the symmetric vibration of the distorted MoO₆ units of polymolybdates

species such as $H_xMo_7O_{24}^{(6-x)-}$ or $H_xMo_8O_{26}^{(4-x)-}$ [29]. After sulfidation (blue spectrum), the signature of the oxide precursors disappears and is replaced by two new bands located at 375 and 400 cm^{-1} , characteristic of the in plane (E_{1g}) and out of plane (A_{1g}) vibrational modes of MoS_2 [30]. The sulfided catalyst spectrum presents a baseline due to Diesel fluorescence and also contains the characteristic vibrations of the coke at 1278, 1358 and 1593 cm^{-1} . These three bands are respectively attributed to poorly organized coke [31], the D-band (observed in amorphous graphite) and the G-band (characteristic of a perfect single crystal of graphite) [32].

((Figure 7))

The MoS_2 phase was detected from around 300 °C. As sulfidation advances, a temporal evolution of the intensity of the 375 cm^{-1} and 400 cm^{-1} MoS_2 lines was observed, with both bands presenting higher intensities with increasing temperatures from 300 °C to 350 °C (Figure 8), interpreted as an increase of the amount of MoS_2 .

((Figure 8))

To summarize, Raman spectra of catalyst pellets were acquired inside a fixed bed HDS reactor under gas-liquid flow, 3 MPa and 350 °C with good enough quality to observe polymolybdates species, MoS_2 and coke bands. As far as we know, such *operando* measurements have not yet been reported.

4. Conclusions

A set-up has been built to perform reactions in a transparent reactor up to 350 °C and 3MPa with an isothermal profile and very good reaction performances. The design makes it possible for the first time to perform Raman measurements of surface of randomly positioned catalyst pellets inside a cylindrical reactor during a gas-liquid-solid reaction thanks to an innovative focalization procedure through the cylindrical reactor. Spectra can be acquired fast enough to follow-up the evolution of the solid phase occurring in a few hours. The set-up has been validated for the Diesel HDS reaction. Interpretation of Raman spectra gives semi-quantitative information on the active phase of the catalyst in representative operating conditions. Next steps will be then to follow up and compare different catalysts evolution during different activation procedures under gas-liquid flow.

Finally, the set-up can be used for a wide range of liquid, gas-liquid or gas-phase heterogeneous reactions such as hydrogenation reactions. A liquid follow-up might be possible with a liquid matrix containing a limited number of molecules so that Raman peaks can be converted to concentration.

Conflict of interest statement: The authors declare no conflict of interest.

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Figure legends

Figure 1 - Principle of the set-up: reactor, heating tube and long working distance Raman objective; a) axial view; b) transverse view.

Figure 2 - Simulated temperature fields of the set up.

Figure 3 – Set up design: (a) reactor placed inside the heating tube, (b) whole set-up inside the Raman device.

Figure 4 – Fluid flow pattern inside the reactor: (a) wet catalyst with gas, (b) immersed catalyst and with some bubbles flowing.

Figure 5 – Laser beam deformation in axial and transverse directions resulting in two focalization points.

Figure 6 – Optical lines in images: positions Z_1 and Z_2 correspond to the beam focalizing on the quartz/fluid interface; positions Z_3 and Z_4 correspond to the beam focalizing on the fluid/catalyst interface.

Figure 7 – Spectra obtained in the reactor under 3 MPa of H₂ inside the reactor at Z_4 in a gas section. Bottom: Oxide state at 25 °C in absence of Diesel; Top: sulfide catalyst (CoMo/Al₂O₃) at 350 °C in presence of Diesel.

Figure 8 - Temporal follow-up of Raman spectra of the MoS₂ active phase as a function of the temperature.

Short text for the table of contents section

A 3 MPa, 350 °C fixed bed reactor has been designed to follow-up gas-liquid reactions on a millimetric size heterogeneous catalyst with Raman spectroscopy. The reactor is a quartz cylinder enclosed in a joule effect heated metal tube. Raman spectra of the solid catalyst and Diesel have been acquired during Diesel hydrodesulphurisation on a CoMo/Alumina extrudate catalyst and show MoS₂ and coke time evolution.