Design, Modelling, and Application of a Low Void-Volume in Situ Diffuse Reflectance Spectroscopic Reaction Cell for Transient Catalytic Studies

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SUPPLEMENTARY MATERIAL

S1. In situ reaction cell operation considerations and suggestions for improvements

1) **Safety:** Upon installation of the reaction cell, safety should be considered for its operation. With the exception of Specac's, most in situ DR cells seldom address safety in their operation. Features such as automatic shutdown, low voltage heaters (<30 V), safety "burst disc" or pressure relief valves, safety shield, etc. should be always considered.[1] The use of ground-fault current interrupters (GFIs) are a must when operating heaters (e.g., cartridge heater to provide heat for the reaction, heating tapes to heat transfer lines) to protect from current leaks which could increase the chance for fire and short circuit.
2) **Pressure gauges:** While most transient experiments will usually occur at ambient pressure, placement of digital pressure gauges (Grainger, P/N 41D947) between 6WV and MFCs to monitor cell pressure can be very useful to ensure consistent pressures from experiment to experiment, also to monitor pressure during leak tests, and to troubleshoot possible clogging of the lines due to sample leaks through the sample mesh.
3) **Sample loading**: The SS 38 μm mesh to hold the sample in the cell is quite thin and may become flimsy, especially after perforating a small hole for the 1/32" thermocouple to pass through. In such a case, we found that using a sturdier second SS mesh of larger opening (~250 μm) to support the smaller 38 μm mesh helped to stabilize it.
4) **Window alignment**: the ZnSe dome possesses an alignment hole to ensure the windows are properly placed in Harrick's HVC reactors to maximize signal throughput. In this new cell design, an alignment pin is not present, therefore one needs to ensure that the two back windows in the dome are parallel to the back side of the reaction cell. The two notches present in the front of the ZnSe window could be also used for alignment and they should be placed parallel to the front of the reaction cell. They also serve the purpose of adding a few millimeters of space while moving the cell up and down to maximize signal throughput while avoiding touching Praying Mantis' top mirrors. Also, it is possible that the front retaining plate would need to be slightly off towards the user to avoid touching the ellipsoidal mirror of the Praying Mantis during such process.

5) **Gas Leaks:** Improper dome placement could result in breaking of ceramic insulating ring. Even when apparently placed well, gas leaks could occur. A standard procedure should include leak checks before cell operation. We have found Restek's electronic leak detector (P/N 22655) to be quite handy for such procedure. There is also a chance that leaks could occur through the joint space between the solid ZnSe window and its metallic support. In such a case, a second O-ring in combination with a modified ceramic ring can fix this problem.
6) **Inline Filter:** It may be advantageous to place a filter after the reaction cell outlet three-way valve to avoid possible contamination of MS with small catalyst powders. This, however, will delay sampling in MS and should be considered during data analysis.
7) **Heat losses:** The current cell design is quite compact and simple, however, as a result the heat cartridges have a fraction of their surface exposed from where heat losses could be significant. A better design should increase the area of contact between the heat cartridges and the bottom of the reaction cell. Alternatively, a cell could be designed where cartridges operate vertically, not horizontally as reported in designs by Dal Santo et al.[2] and Vannice[3] or that utilizes coiled heaters around the sample cup such as that reported by Schubert et al.[4] Such modifications could improve heat transfer and increase the temperature of operation in the cell.

   We recently reported that with a similar window/dome shape, the dome could reach temperatures as high as 150 °C.[5] This is likely the case for the ZnSe windows used in the reaction cell. To extend its life, cooling of the top of the cell next to the dome metal frame (e.g., via the retaining plates) could be devised to extend its life.[1] Such modification should avoid disturbing the IR beam path or scratching the mirrors optics.
8) **Cell inertness:** while the cell is made of corrosion-resistant SS 316/316L, there is a chance that upon repeated use and more likely if sample is calcined in situ at high temperatures, that the cell wall will become oxidized. A standard procedure should therefore involve blank run tests to ensure the inertness of the cell prior to reaction. An additional preventative measure is the silanization of the cell prior to use with services such as those provided by SilcoTek company (https://www.silcotek.com/).

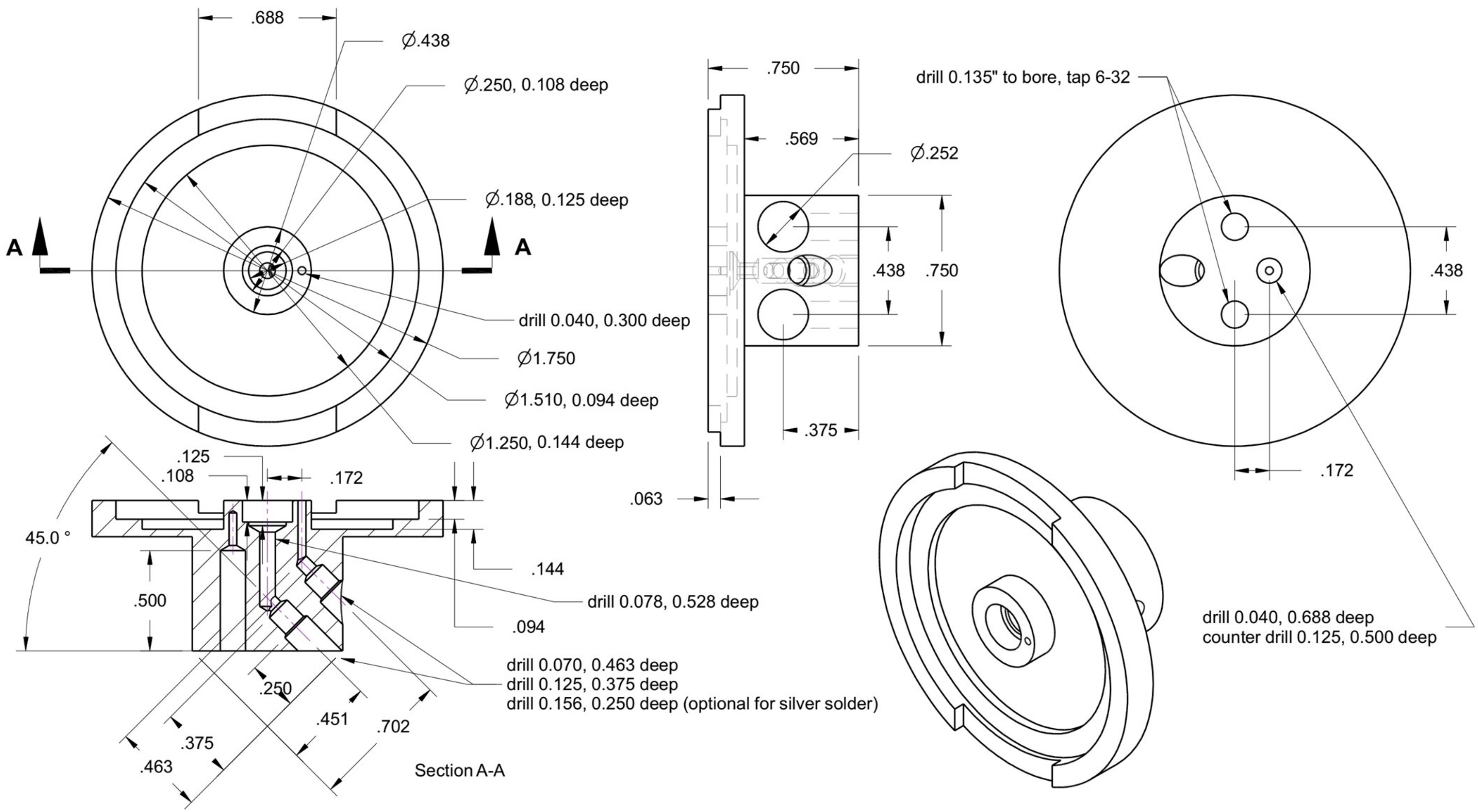

Figure S1. Blueprint of main reaction cell body (9 in Fig 1).

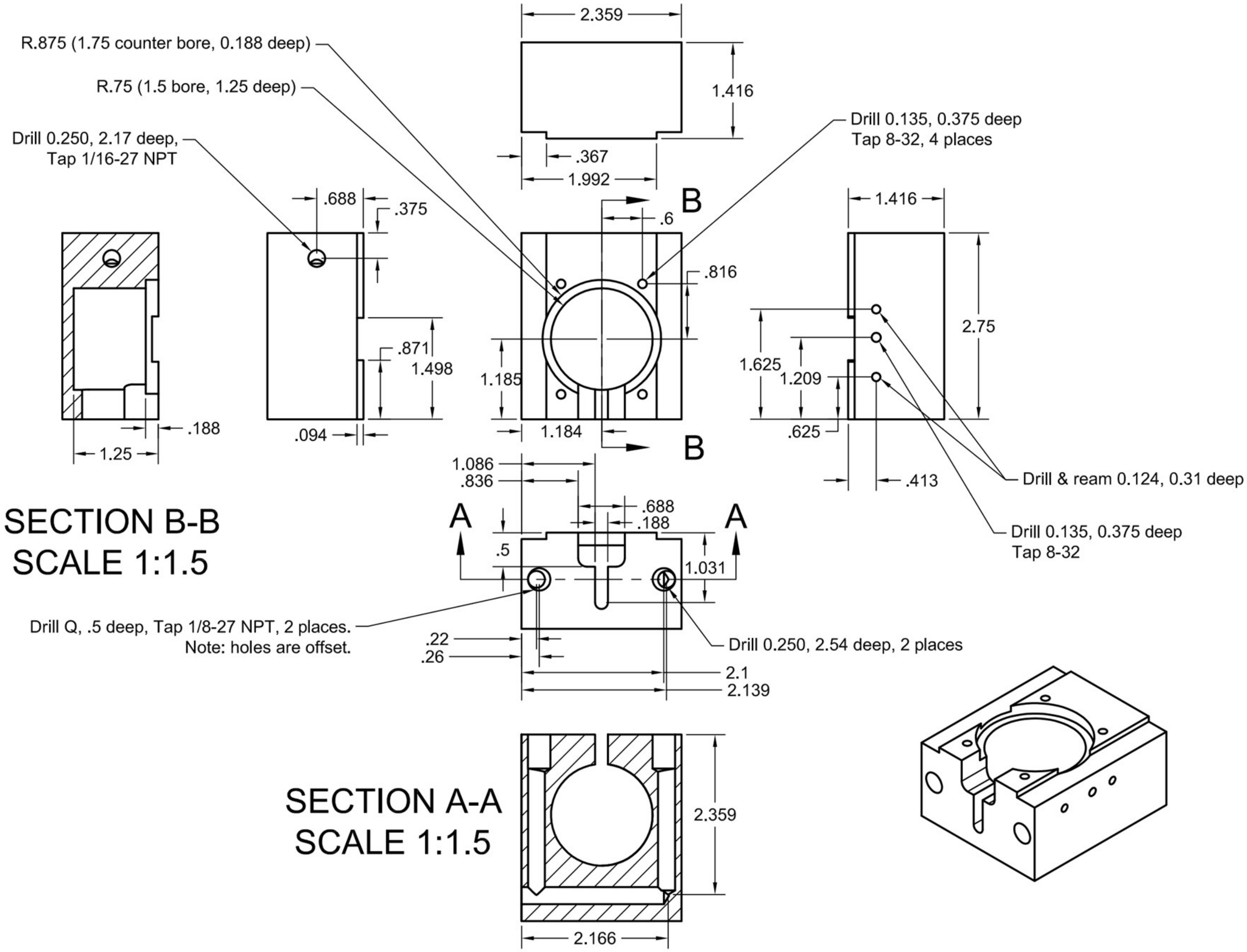

Figure S2. Blueprint of reaction cell housing (7 in Fig. 1).

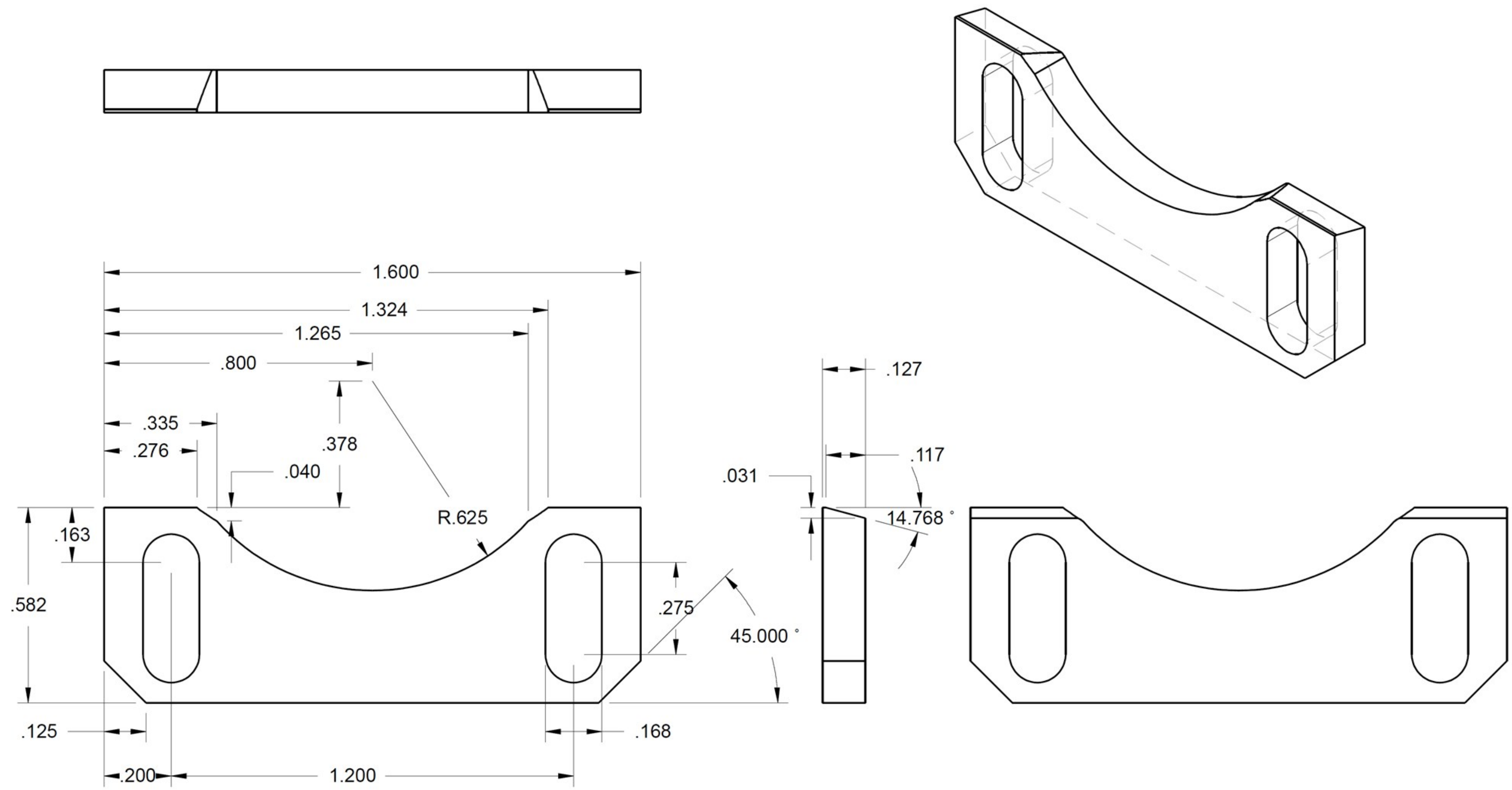

Figure S3. Blueprint of retaining plates (13 in Fig. 1).

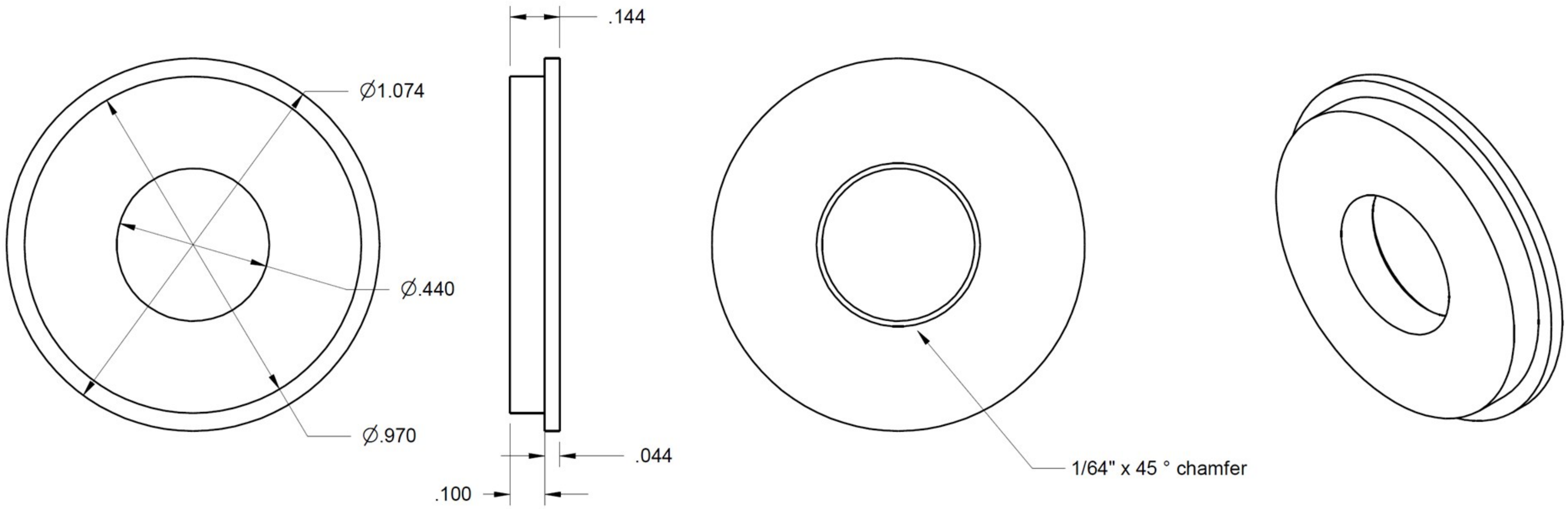

Figure S4. Blueprint of insulating ceramic ring (10 in Fig. 1).

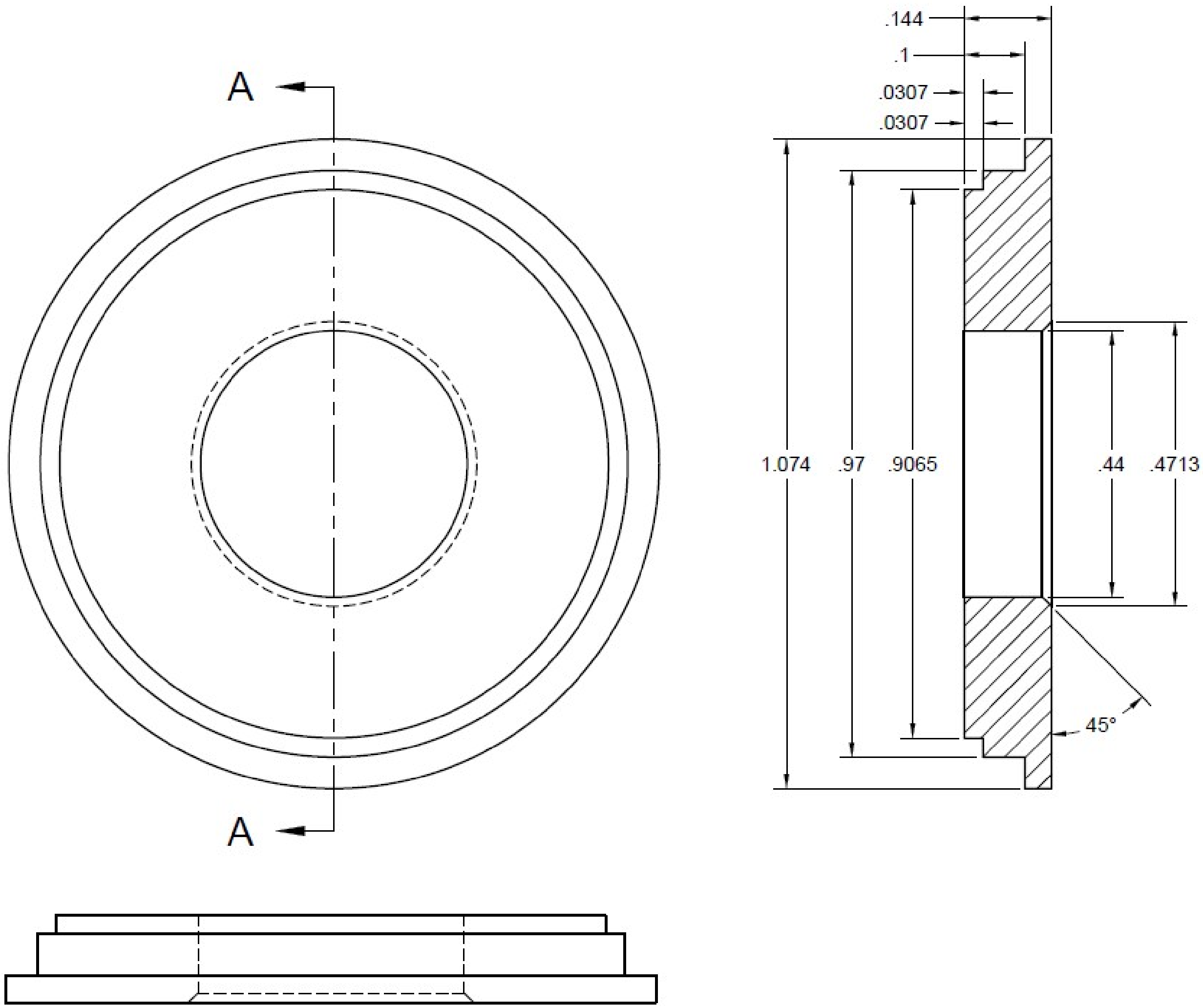

Figure S5. Blueprint of alternative insulating ceramic ring (10 in Fig. 1). For use along with silicone O-ring (23 mm ID x 25 mm OD, McMaster-Carr, P/N 5233T121) in the case of leaks through the IR ZnSe dome.

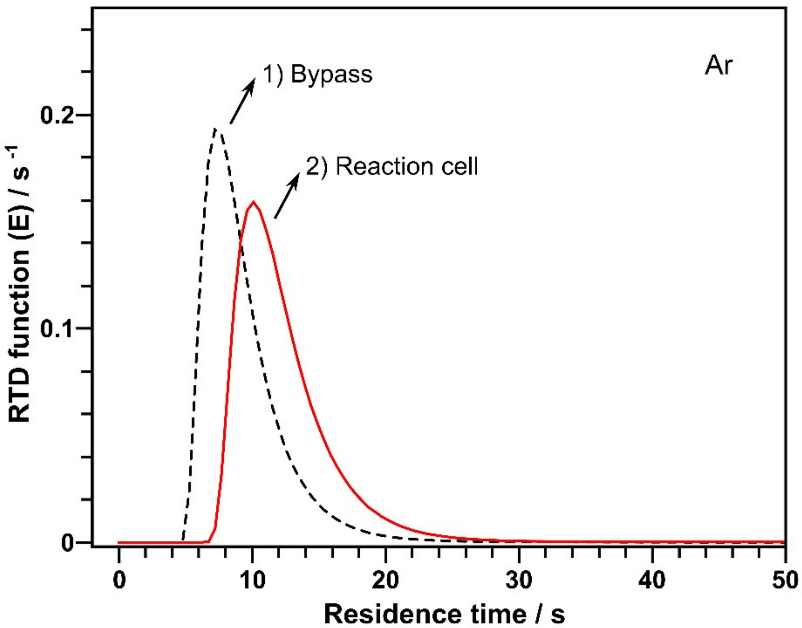

Figure S6. Residence time distribution (RTD) profiles of Ar gas pulse through the bypass (trace 1) and the reaction cell (trace 2). Conditions: ambient temperature, 1 atm, 50 μL loop, He carrier flow of 45 std cm^3/min.

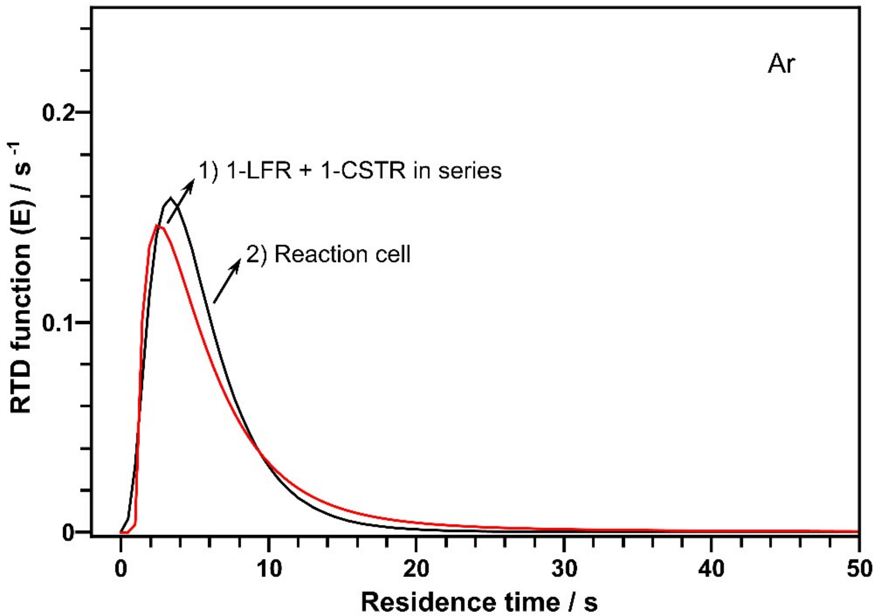

Figure S7. Residence time distribution (RTD) profiles of Ar gas pulse through the reaction cell (trace 2) and corresponding fitted RTD two reactor model of one laminar flow reactor in series with one CSTR reactor (trace 1). Experimental residence time distribution data were offset to zero by the corresponding $\tau_{p,r}$. Conditions: ambient temperature, 1 atm, 50 µL loop, He carrier flow of 45 std cm^3/min.

S2. Two ideal reactors in series: case of LFR + CSTR of equal volume

The solution to the RTD function of one LFR and one CSTR in series was derived by following a method similar to that described in Reference [6] in combination with a symbolic solution provided by Maple software:

$$E(t) = \begin{cases} 0, & t < \frac{\tau_1}{2}; \\ k_2 \exp\left(\rho - k_2 t\right) + k_2 \rho \exp\left(-k_2 t\right)\left[Ei\left(k_2 t\right) - Ei(\rho)\right] - \frac{\rho}{t}, & t \geq \frac{\tau_1}{2}. \end{cases}$$

Where:

τ_1 = residence time in the LFR in s

τ_2 = residence time in the CSTR in s

$$\rho = \frac{\tau_1}{2\tau_2},\ k_2 = \frac{1}{\tau_2}$$

And Ei is the exponential integral function

The best fitted parameter values were found to be: $\rho = 0.309$, $k_2 = 0.326\ s^{-1}$

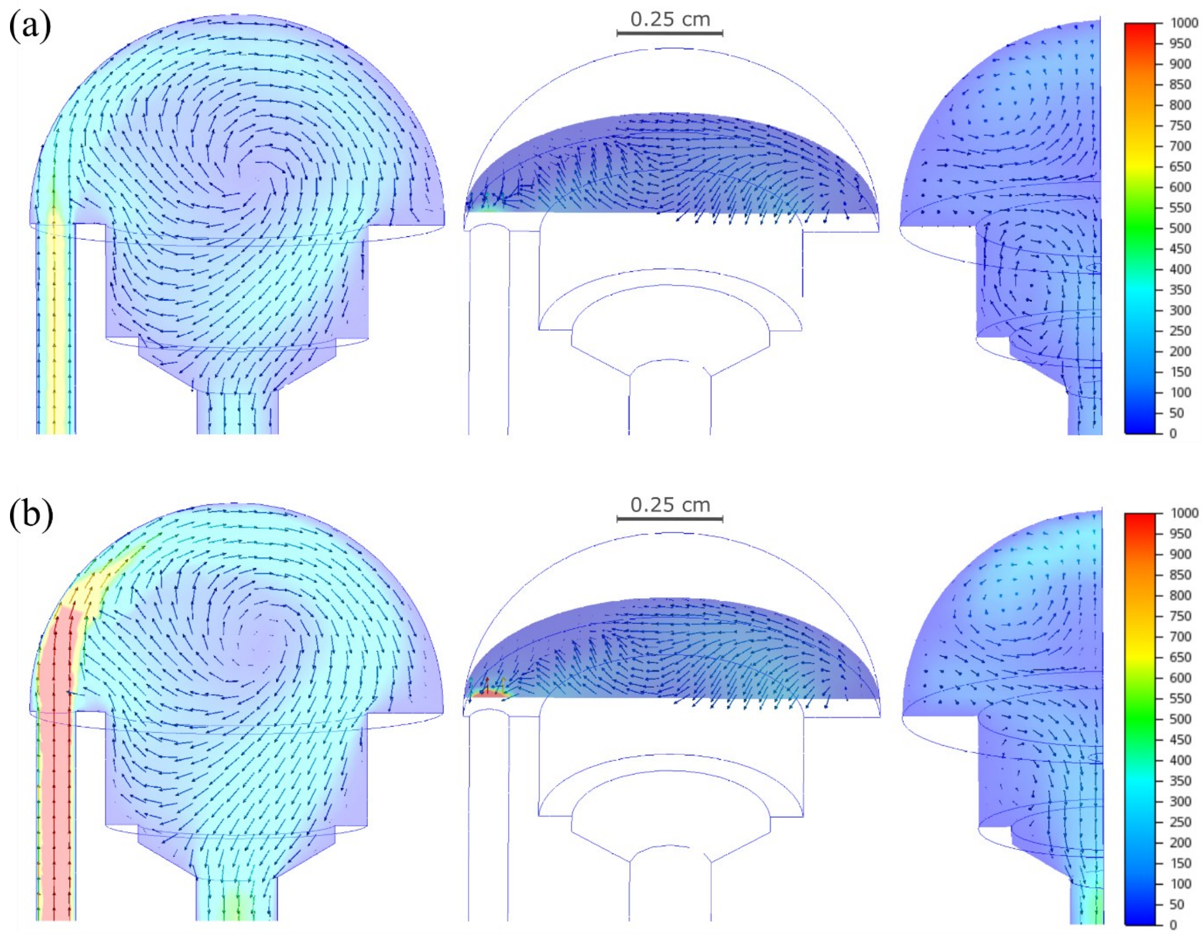

Figure S8. Reaction cell CFD simulation of velocity magnitude (in cm/s). Conditions: He gas, 25 ºC, outlet pressure (gauge) of 0 Pa, and volumetric flow to cell of: (a) 45 cm^3/min and (b) 180 cm^3/min. Left figure: side view of vertical plane at cell center point; middle figure: top view of horizontal plane at approximately 0.5 mm above sample cup edge; right figure: front view (with respect to flow inlet) of vertical plane at cell center point.

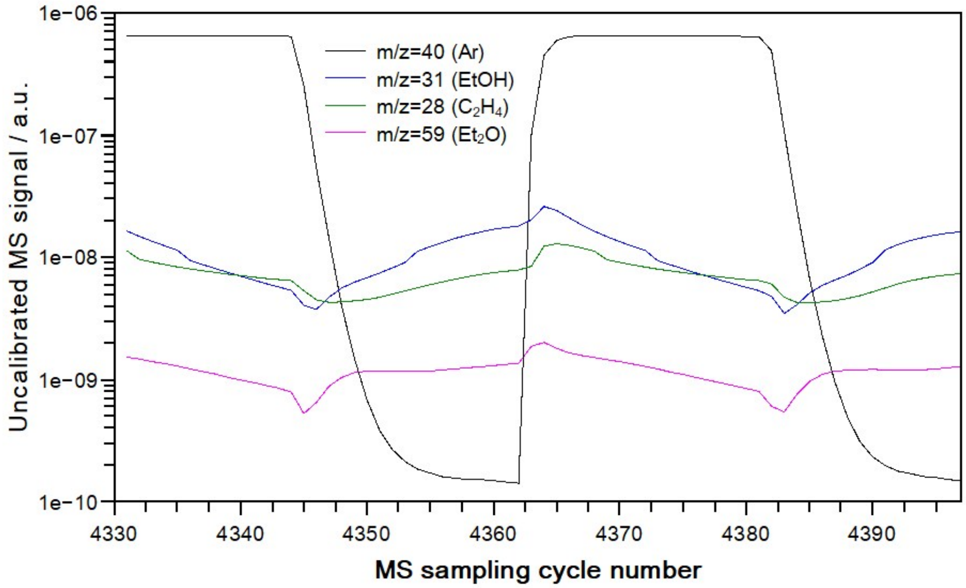

Figure S9. Online MS signals during two feed modulation cycles at ethanol dehydration conditions on γ-Al_2O_3 in in situ cell. Conditions: 200 ºC, 1 atm, feed modulation from He/Ar → He+EtOH (1 kPa), modulation frequency = 1/90 Hz, total gas flow ~45 std cm^3/min. Ar signal shows square-like waveform modulation.

References

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