

# Evaluation of the Two-Dimensional Performances of Low Activity Planar Catalysts: Development and Validation of a True Scanning Reactor

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**Supporting Information** 

**ABSTRACT:** The development of a scanning reactor for planar catalysts is presented here. With respect to other existing models, this reactor is able to scan catalysts even with low turnover frequencies with a minimum sensed circular area of approximately 6 mm in diameter. The downstream gas analysis is performed with a quaprupole mass spectrometer. The apparatus performances are presented for two different reactions: the hydrogenation of butadiene over palladium films and the oxidation of CO over a gold/titania catalyst. With the final setup, true scans in both X and Y directions (or even in a previously defined complex directional pattern) are possible within a scan speed ranging from 0.1 to 5.0



mm/min. Finally, this apparatus aims at becoming a valuable tool for high throughput and combinatorial experimentation to test patterned active surfaces and catalytic libraries.

**KEYWORDS:** high throughput experimentation, heterogeneous catalysis, scanning reactor, catalyst libraries

• ombinatorial chemistry has shown a significant increase in → its impact across many industrial and academic fields, from the pharmaceutical sector through fine chemicals, plastics, oil products, material science, and heterogeneous catalysis.<sup>1-7</sup> In this last field, the utilization of a combinatorial approach through pragmatic high throughput experimentation (HTE) allows for a substantial decrease in the requested workload to obtain the best (or at least an improved) catalyst. In addition, the continuous and massive development of advanced statistical tools (such as the design of experiment-DoE and other multidimensional data treatments) now allows for combining complex data sets from different sources, thus yielding a deeper understanding of the properties of new materials.<sup>4</sup> In this context, the availability of suitable analytic tools is mandatory to feed this complex machinery with robust and reliable data sets.<sup>5</sup> HTE methodologies are largely used in heterogeneous catalysis, and several reviews are available.<sup>6–11</sup> Different analytical strategies are proposed using parallel reactors<sup>11-13</sup> or scanning reactors. Generally, the latter ones are applied on flat catalysts, and only a few examples are available for real continuous scanning systems. A good approach lies in the synthesis of discrete areas of active samples, spatially isolated between each other, which are tested one-by-one by a movable head.<sup>14,15</sup> Real, spatially resolved tests are reported using capillary glass probes: the reaction takes place under the probe that samples the product gases and drives them to a downstream mass spectrometer.<sup>16-19</sup> The last cited work shows a quite interesting configuration that can be successfully used with high-activity surfaces. If highly active catalysts are tested, constraints related to reactants gas feed concentrations and to the minimum sensed area are quite mild; therefore, it is possible to reach spatial resolutions down to 250  $\mu$ m with feeding gas concentrations up to 5%.<sup>19</sup>

As we will show later, if medium-to-low activity surfaces are tested, the apparatus constraints become difficult to comply with the consequence that the feeding gas mixture must be diluted (down to hundreds of ppm) and the sensed area must be enlarged to observe sufficient reactivity. In this work, we present the development of an apparatus that addresses these problems, i.e., which is able to test with high sensitivity planar catalysts possessing medium-to-low activities. In particular, we tested a Pd film catalyst on the selective hydrogenation of 1,3butadiene to butene and a Au/TiO2 powder catalyst on the oxidation of CO to CO<sub>2</sub>. Both of these catalytic systems are known to have medium-to-low activities with turnover frequencies ranging from 4 to 10 s<sup>-1</sup> and from  $9 \times 10^{-6}$  to 4.5 s<sup>-1</sup> for Pd and Au/TiO<sub>2</sub> catalysts, respectively.<sup>20-23</sup> The system presented here is able to spatially scan a planar catalyst and test its catalytic activity continuously following any desired preset pattern. With respect to our previous system for planar

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surfaces,<sup>24</sup> we completely redesigned the reactor probe to solve most of the technical problems previously encountered and to improve the overall efficiency. In fact, previous prototypes had a rough and nonhomogeneous temperature control, did not allow for real scans, and showed poor-to-null sensibilities relative to the detection of  $Au/TiO_2$  reactivity. All of these points will be discussed in depth in this paper. The redesigned apparatus is now able to truly scan the reactivity of planar catalysts over both the *x* and *y* axes. Finally, a tentative modeling of the probe capability next to the MS data handling is proposed.

**New Reactor Probe Design Achievements.** The core of the scanning catalytic reactor for planar surfaces (SCR-PS) is the reaction chamber defined by the reactor probe and by the planar catalyst surface as shown in Figure 1a. A true scan is



Figure 1. (a) Overall scheme of third generation reactor probe and (b) side and bottom view of the terminal part.

possible only if the reactor head never touches the catalyst surface, not forgetting that reactants and product should be confined in some way in a well-defined volume. According to the conceptual basis of the controlled leakage system, this is achieved through the correct design of the probe head, through a fine balance of the head vs surface distance, and of the inlet vs outlet gas flows. In particular, the annular surface of the outer body of the probe (which is very close to the catalyst surface) and the adjusted outlet gas flow ensure good local insulation of the reaction chamber. From another point of view, the combination of this annular surface and the settings of gas flow allows for fine control of the leakage to or from the inert outer environment (the "gas-cushion" sealing system).

This completely novel design was necessary to solve the problems encountered with our previous prototypes. Technical details regarding these issues are discussed more in depth in the Supporting Information. Here, we will only address the main results of such improvements.

The optimized probe geometry (Figure 1b) increases the catalytic conversion through a better contact between reactants and the catalytic surface. The gases from the small 0.5 mm diameter central hole are forced to pass over the catalytic surface before being aspirated by the outlet port. This is possible because the gases from the central nozzle are maintained in close contact with the catalyst surface for a diameter of 4 mm below the inner part at the same quota level of the outer one. As will be described later, the true area sensed by the SCR-PS is ~28 mm<sup>2</sup>. This means that the true diameter sensed by the SCR-PS is ~6 mm. This interaction area is large enough to test the activity of catalytic systems with low turnover frequencies.

We placed the heating cartridge inside the gas flow, providing an extensive and direct contact surface between reactants and the heating cartridge. Therefore, the gas is preheated inside the inner probe body. Moreover, an internal mixing chamber filled with small glass beads was created above the nozzle. Exploiting their large surface/volume ratio, it is possible to ensure a very efficient and homogeneous thermal distribution between the probe and the gas. With this solution, reactants are perfectly thermalized at the probe temperature.

Finally, the new symmetric design ensures homogeneous sampling both in static mode and during the scan movement in every direction. Accordingly, the cavity arrangement with the lined-up IN-nozzle/annular-OUT allows a true 2D scan free of artifacts due to the scanning direction. As we will show later, this modification on the reactor probe improved the performance of the scanning reactor not only in terms of absolute sensitivity but also in terms of scanning capability.

**Evaluation of the Controlled Leakage Performance.** The leakage performance was carried out to evaluate the inner gas dilution (which ultimately has a significant impact on the system sensitivity) and to finely tune the probe/catalyst gap. The overall signal profiles of the test are reported in Figure 2.



**Figure 2.** (a) Probe/catalyst gap vs time at the following stepwise values: 12, 21, 30, 42, 62, 80, 122, 160, and 201  $\mu$ m, and (b) related normalized Ar and N<sub>2</sub> MS signals vs time along (1) 100% N<sub>2</sub> signal, (2) 100% Ar signal, (3) probe position settle and MS online connection, and (4) fine probe movement on the Z axis (21–201  $\mu$ m).

With a probe/catalyst gap equal to 12  $\mu$ m, we recorded a 14% mixing level of the outer gas  $(Air/N_2)$  in the inner one (Ar). This mixing level progressively increases as the distance from the surface increases, reaching approximately one-half (46%) at the maximum tested gap. As expected, the controlled leakage system guarantees the best insulation at smaller distances, where it is possible to recover nearly 90% of the gas. Even at low gaps, the system shows a good stability, but small changes on the Z axis cause significant signal fluctuations. This behavior is already known and can be used to control the distance gap using feedback logic.<sup>19</sup> With respect to our previous prototypes, the general improvements applied to the probe design caused significant enhancement in terms of gas recovery percentage, which in turn enhances the overall sensitivity. The operational conditions for this test were close to the ones used in the catalytic tests, where the probe was placed at 50  $\mu$ m from the catalyst surface, therefore, with  $\sim$ 30% gas dilution. As a final consideration, it should be noted that the performance of the controlled leakage system can also vary passing from isokinetic



Figure 3. Catalyst schemes of (a) Pd film on a Si slide and (b) Au/TiO<sub>2</sub> powder on a partially coated aluminum slide. All of the measurements are in mm.

to nonisokinetic conditions. As an example, if contaminations from the outer environment should be avoided, the inlet gas flow can be substantially increased (maintaining the outlet flow constant) to decrease back diffusion of contaminants. On the other hand, if it is necessary to avoid unsensed areas of the catalyst from coming in contact with reactants spilling out from the probe, the outlet flow can be increased. The catalytic tests on Pd films that will be presented in the next section represent a good example of this concept. In our previous work,<sup>24</sup> we observed that Pd film catalysts show a significant deactivation under working conditions. Therefore, we decided to move from isokinetic conditions to an increased uptake of 1.5 mL/min. Taking into account the dilution factor, we determined that under these conditions the gas recovery was ~70%, working at a distance of 50  $\mu$ m.

**Catalytic Tests.** To prove that the new instrumental design is capable of spatially resolving the catalytic activity of a planar catalyst under scanning conditions, we choose two well-known reactions: the hydrogenation of 1,3-butadiene on a Pd film<sup>24,26,27</sup> and the oxidation of CO to  $CO_2$  on Au NPs supported on TiO<sub>2</sub> powders.<sup>28</sup> The basic schemes of the two catalyst are reported in Figure 3. Along with the purpose of using them in this paper, these catalytic reactions are seen as well-known systems to test reactor capabilities but not vice versa. We decided to also test a powder catalyst (Au/TiO<sub>2</sub>) to check the reactor's capability on more complex surfaces that mimic a patterned powder-coated surface (more attractive for industrial applicative studies rather than metallic thin films).

**Hydrogenation of 1,3-Butadiene on a Pd Film.** MS signals for 1,3 butadiene (reactant) and butene (product) are reported in Figure 4. The channel related to butane at m/z = 58 is not reported because no formation of butane was observed. Signal trends highlight qualitatively a good sensitivity over the surface and a net increase of catalytic conversion recorded on the edges of the active areas regardless of the scan speed.

The data recorded by the MS system were modeled to correctly evaluate the area sensed by the probe. In fact, we have to consider that, as our reactor works in controlled leakage conditions, no physical constraints are used to define the sensed area. This information may be extracted from the previously shown activity plots through a sequence of several simple steps (Figure S4).

Let us start with a preliminary consideration: if the sensed area is infinitely small, we would have recorded a staircase reactivity profile as the catalytic surface steeply changes from active to blank/inactive along the X axis (Figure 3). Because the reactor probe instead has finite dimensions, the shape of the reactivity profile cannot be a staircase. To model it, we propose



**Figure 4.** Normalized MS signal for 1,3 butadiene (reactant, 54 amu, black) and butene (product, 56 amu, red) as a function of time for three different scan directions and speeds (dark gray = active area; light gray = not an active area). SCAN 1: 0.2 mm/min; SCAN 2: 0.4 mm/min; and SCAN 3: 0.8 mm/min.

a simple but reasonable model (Figure S5). We assume that the sensed area is circular and that the normalized activity is 1 or 0 when all of the sensed area is on the active or blank surface, respectively. For all the intermediate situations, i.e., when the probe is passing from the active to the blank surface, the activity is calculated as the ratio between the sensed area that is actually on the active part and the total sensed area. The parameter that we would like to fit is the diameter of the sensed area. The real probe model describes the steps of the staircase profile as a quasi-sigmoid function where higher slopes correspond to a small probe diameter and all of the probe sets intersect on the edge at a value of 0.5.

Here, we presented the model to scan at a speed of 0.8 mm/ min. The sampling rate is 0.2 mm/point due to the fixed MS sampling time (4 pts/min). The raw data shown in Figure 5a are collected across the edge (which is located at x = 22 mm) from the blank surface to the active one. From these raw data, a sigmoid shape on signals of both reactant and product is clearly visible. On both profiles, a mathematical fitting with a sigmoid Boltzmann function is tentatively applied and also reported in Figure 5a. To compare the data with the scan model, the Boltzmann sigmoid functions are normalized in the range 0–1.



Figure 5. (a) Raw MS signals for 1,3-butadiene (blue) and butene (black) on a scan range of 17-29 mm with the Boltzmann sigmoid fitted on the data in red and the theoretical staircase step in green. (b) Scan model calculated for probe diameter quasi-punctiform (black), 0.5 mm (red), 4 mm (orange), 6 mm (blue), and 8 mm (green) for butene. The Boltzmann sigmoid calculated on real data is the dashed magenta line.

In Figure 5b, the data of products are compared to the set of model probe diameters.

The scan model for a probe diameter of 6 mm fits well with the test data around the central part of the sigmoid: the slope of the two curves are rather similar (1.13 vs 1.00) and strongly differ from the others. We could then suggest that the true area sensed by our reactor probe is close to 6 mm in diameter around the central inlet gas nozzle. This diameter leads to a sensing area of ~28 mm<sup>2</sup> and corresponds to the size of the gas expansion chamber under the probe closed by the leakage system.

Finally, it is interesting to note that we have also determined that a change in the scan speed affects the slope of the sigmoidal curve in the time domain only (as could obviously be expected), whereas this does not happen if the data are reported in the spatial domain. This means that the response time of the whole apparatus is sufficiently fast to correctly follow the activity of the underlying catalyst without introducing unwanted instrumental artifacts.

**CO** Oxidation on Au/TiO<sub>2</sub>. This kind of test was unsuccessfully performed using the second generation reactor head (not published) probably due to the lower sensitivity of that prototype. However, the catalyst activity was proven by a flow test of the powdered catalyst on a conventional gas flow reactor. In Figure 6 is shown the reaction profile recorded on the same powdered catalyst dispersed on a planar sample holder as described in the Experimental Procedures. The MS signal on mass channel 44 (CO<sub>2</sub>, product) increases rapidly when the probe moves from the blank site A (aluminum) to the catalytically active Au/TiO<sub>2</sub> site B. The first run was performed at 80 °C at a relatively high scan speed of 1 mm/min (from 5 to 20 mm). At this temperature, a net increase (~41%) in the CO<sub>2</sub> signal is detected.

The temperature is then increased to 100 °C in a stationary position, and we observe another increase ( $\sim 6\%$ ) of the MS signal. In this way, we have also proven the ability of the apparatus to detect changes in activity due to temperature changes. At this point, we then performed the back scan (from 20 to 5 mm) at a slower scan speed (0.5 mm/min). Also in this case, the system was able to detect the decrease of the activity, recovering the values detected at the beginning of the initial scan (inactive surface).



Figure 6.  $CO_2$  (44 amu) MS signal vs time along the oxidation catalytic scan tests over Au/TiO<sub>2</sub>.

We have shown in this study that the apparatus developed is able to sense the reactivity of different types of surfaces and in different types of reactions. The sensed area was optimized to observe the reactivity of catalysts with low turnover frequencies. Of course, if catalysts with higher turnover frequencies are studied, a reduction of the sensed area through a scale down of the reactor probe is possible. The catalytic tests carried out on model specimens show the potentiality and flexibility of this apparatus to test the planar catalytic activity of discrete sample arrays from film or coated systems. These methodologies should be part of a screening process or activity HTE procedures for new coating materials. In particular, a relative comparison of surfaces with different activities is always possible, and the quantification of absolute activities is possible through a calibration against reference planar catalysts. Finally, the modular design of the apparatus allows a simple replacement of the head probe. With properly designed heads, other applications, such as photocatalytic tests and/or surface modifications, can be foreseen.

## **EXPERIMENTAL PROCEDURES**

Apparatus Design and Setup. The apparatus is composed of three parts (Figure S1): the heated steel reactor probe, the heated aluminum sample holder (mounted on a motorized XYZ stage), and the sealed PMMA box that encloses the previous two parts and ensures a controlled, slightly overpressurized, inert environment (Ar). Even in this third generation prototype (for sake of comparison, prototypes 1 and 2 are described in ref 24 and in Figure S2), the gas reactant mixture is driven onto the active surface, where the reaction takes place through the reactor probe: the inert gas cushion around it avoids the gas dispersion from the interaction volume defined by the probe and the underlying surface. In the meantime, the controlled leakage dilutes the product gas mixture extracted by the OUTLET manifold and driven to the QMS analyzer. With respect to previous models, the new reactor probe is now bigger (13 vs 7 mm outer diameter; see Figures S2 and S3) and made of two parts (an outer and inner body, Figure 1a). The increase of the overall size was necessary to raise the sensed surface from 12.5 to 28.3 mm<sup>2</sup>, thereby improving the apparatus sensitivity. The two pieces are designed and assembled together to obtain on the bottom piece a concentric system centered on the inlet nozzle and surrounded by an annular cavity (with the top piece having the outlet gas port, Figure 1B). The internal part of the probe drives over the catalyst surface the feeding gas mixture, which is heated by a heating cartridge inserted from the top. The  $30 \times 3$ mm internal mixing chamber is filled with small glass beads (d= 1 mm just above the 0.5 mm restriction of the final nozzle to improve the heating efficiency. The heating temperature is controlled by a thermocouple and a digital controller (Eurotherm 808). The gas product mixture is sampled by the annular manifold, which is connected to a quadrupolar mass spectrometer (HIDEN-HPR20) by a common jet-separator interface.

Relevant changes were also applied on the sample holder system, which in our previous publication was not able to perform a true scan because neither the X nor the Y axes were motorized. In the apparatus presented here, the XYZ stage is motorized with three stepping motors controlled by unique user-made hardware, which in turn is driven by LabVIEW-based software. On the X and Y axes, the movement resolution is 10.4  $\mu$ m/step and the Z axis is 2.94  $\mu$ m/step. The fine gap between the active-surface and the reactor-probe on the Z axis is measured by a dial test indicator (MITUTOYO lever type, 513 series, 0.50/0.01 mm) placed next to the probe. The Z reference system is tuned prior to every test at the same temperature used for the test itself. A short comparison between our design and other reported configurations is described in the Supporting Information.

**Catalyst Preparation and Test.** To test the performance of the scanning reactor, we used two conceptually different active materials not homogeneously distributed over flat surfaces: (i) a planar metal nanostructured Pd film and (ii) a powder catalyst gently spread to coat a suitable sample holder.

The first specimen was a 20 nm thick palladium film deposited on a  $10 \times 30$  mm silicon slide, obtained using methodology reported elsewhere.<sup>25</sup> This system was already tested in our previous work with a different reactor design in the selective hydrogenation of 1,3-butadiene and is used here for comparative purposes.<sup>24</sup> To obtain active areas placed next to reference/inactive ones, we ablated Pd from the central part

of the slide only, thus creating a  $7 \times 10$  mm inactive area (Figure 3a). A laser ablation system (New Wave mod. UP266; optimized conditions: 30 mJ/cm<sup>2</sup>; spot size: 50  $\mu$ m) was used for this purpose. We decided to use a single modified slide instead of a combination of a Pd film slide and a Si blank reference placed side by side to avoid noisy MS signals. Indeed, in preliminary experiments with this configuration, we were never able to achieve a perfect alignment on the z-axis of the two slides. In this situation, the high sensitivity of the system to the distance gap generates several artifacts on MS signals.

The reaction mixture was composed of 1,3-butadiene at 416 ppmv and hydrogen at 833 ppmv in helium carrier gas. The reaction was monitored by mass spectrometry on channels 54 amu (1,3-butadiene), 58 amu (butane), 2 amu (hydrogen), 56 amu (butene), 20 amu (argon), and 4 amu (helium). After placing the sample on the sample holder, the PPMA box was hermetically closed, and the internal environment was outgassed with Ar at a high flow rate (1 L/min). The planar Pd film catalyst was then pretreated in situ with  $H_2$  (5 mL/min) at 100 °C slowly sweeping the surface at 0.6 mm/min over the whole investigated path. The catalytic tests were performed at 100 °C, positioning the probe 50  $\mu$ m from the surface. The input/output flow rates were set at 1 and 1.5 mL/min, respectively. The surface was scanned several times at different speeds. MS signals for 1,3 butadiene (reactant) and butene (product) are reported in Figure 4.

The second specimen is a powder Au/TiO<sub>2</sub> (3% w/w Au loading) catalyst prepared by aqueous impregnation on commercially available TiO<sub>2</sub> (titanium dioxide nanoactive; particles size diameter: 5–20 nm). After calcination of 1g of TiO<sub>2</sub> in air for 1 h at 500 °C, the support was impregnated with an aqueous solution containing 52 mg of HAuCl<sub>4</sub> and stirred for 2 h. The catalyst precursor was dried in air at 80 °C overnight and then reduced in flowing H<sub>2</sub> at 500 °C for 1 h. The activity of the so-prepared Au/TiO<sub>2</sub> catalyst was preliminary checked in flow conditions at 80–100 °C in the oxidation of CO to CO<sub>2</sub> as a model reaction.

The powder was then dispersed in acetone to obtain a slurry and rubbed accurately on a proper drip tray  $(11 \times 15 \times 0.5 \text{ mm})$  dug on an aluminum slide. After drying slowly overnight, a compact powder film was obtained on the sample holder. The exceeding powder was shaved off using the edge of a ceramic glass cutter. The resulting surface is flat at the micro scale (Figure 3b). The oxidation reaction was performed in a similar manner as described above (50  $\mu$ m distance gap and scan speeds of 1 and 0.5 mm/min) for the hydrogenation. CO (500 ppmv) and O<sub>2</sub> (5%) in helium were used as reactants and carrier gas, respectively. The reaction was followed by monitoring the mass channels 28 (CO), 32 (O<sub>2</sub>), 44 (CO<sub>2</sub>), 20 (Ar), and 4 amu (He). Helium was used to correct instrumental drifts. The Au/TiO<sub>2</sub> catalyst is active without any in situ pretreatment.

Both specimens are intended to mimic and model a catalytic library for thin films and coated surfaces for screening analysis.

**Evaluation of the Controlled Leakage Performance.** The performances of the controlled gas leakage system were evaluated in isokinetic conditions, i.e., using an inlet Ar flow (1.5 mL/min) equal to the outlet flow. The outer gas was air at atmospheric pressure and room temperature. To evaluate the dilution degree of the inlet gas (Ar), we monitored the outlet gas mixture by a QMS analyzer on mass channels 20 (Ar<sup>2+</sup>) and 28 amu (N<sub>2</sub><sup>+</sup>). The nitrogen signal of air, together with the decrease of the Ar signal, are used to quantify the mixing

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between the outer and inner gases. We proceeded as follows: (1) first, we recorded the signals with the inlet Ar closed (these signals are representative of 100% leakage); (2) we then recorded the signals of Ar bypassing the reactor probe (these signals are representative of 0% leakage); (3) the probe was then placed 12  $\mu$ m from the substrate and, after bringing the reactor probe online, the inlet/outlet flows were balanced; (4) the gas leakage trend was then followed varying the probe/ catalyst gap stepwise from 21 to 210  $\mu$ m. The results of this test are reported in Figure 2.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscombsci.5b00103.

Overall apparatus photo, scanning reactor evolution line, workflow of the data handling, and schematic representation of the simple scan model presented (PDF)

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#### **Author Contributions**

M.M., S.R., and L.O. conceived and designed the experiments. M.M., A.N., and L.O. performed the experiments. M.M. and S.R. analyzed the data. C.D., V.d.S., R.P., and D.M. contributed reagents, materials, analysis tools, and/or discussion. M.M., A.N., and S.R. co-wrote the article and Supporting Information.

#### Notes

The authors declare no competing financial interest.

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