OPTIMISING CATALYST SELECTION

Marlene Führer, Daria Otyuskaya, Maria de la O Masa Lorenzo, Rodrigo Duarte Oliveira Silva, Francisco Maroto de la Puente, and Tiago Vilela, Avantium R&D Solutions, provide the results of a comparative study testing commercial acetylene hydrogenation catalysts, which highlights the importance of catalyst selection in line with plant requirements.

Selective acetylene hydrogenation is a critical process in the petrochemical industry, primarily used to purify ethylene streams by removing trace amounts of acetylene. Acetylene is a highly unsaturated compound that can poison downstream polymerisation catalysts and degrade the quality of polyethylene. Therefore, it is essential to reduce the acetylene content in polymer-grade ethylene to acceptable levels (typically below 5 ppm) through selective hydrogenation.

Acetylene conversion units (ACUs) are essential for purifying polymer-grade ethylene in steam cracker plants. These units come in various designs depending on where the acetylene hydrogenation reactor is situated. The two primary configurations are generally referred to as front-end and tail-end (or back-end).[1] Regardless of their placement, the common goal is to selectively hydrogenate acetylene.

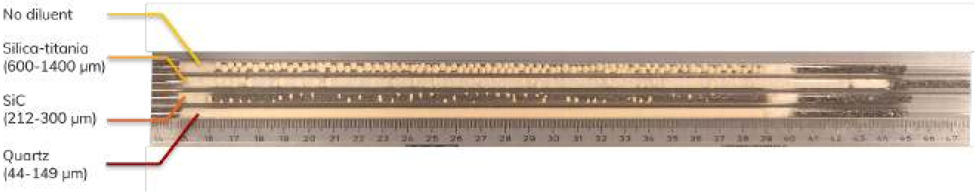

Figure 1. Image of a filled single-pellet-string quartz reactor to visualise the reactor loading of the spherical shaped catalysts.

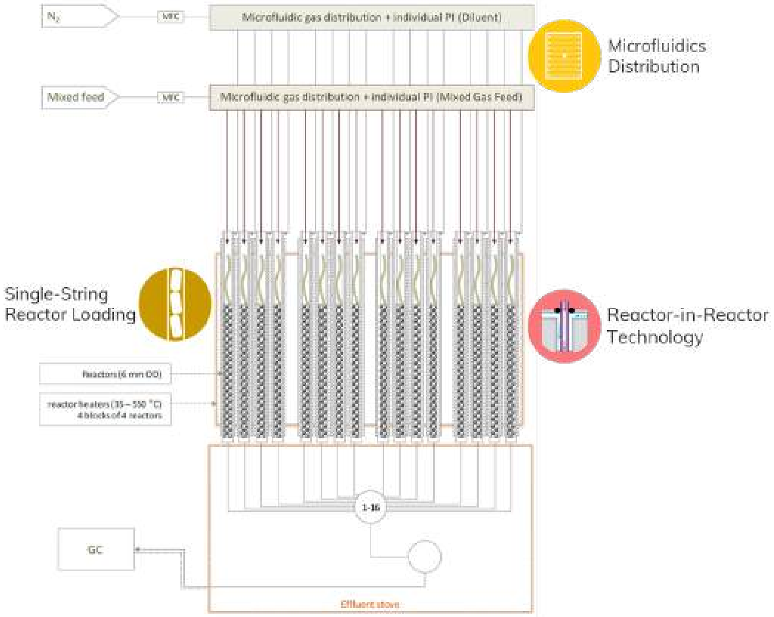

Figure 2. Schematic of the 16 reators Flowrence unit, configured to evaluate the performance of acetylene hydrogenation catalysts.

Acetylene hydrogenation in fixed bed catalytic reactors is widely used in refining processes. Fixed bed reactors allow selective hydrogenation of acetylene to ethylene without over-hydrogenation to ethane. However, ethylene can also hydrogenate to ethane, reducing selectivity. Additionally, heavy hydrocarbons can also be formed from liquid and solid parts known as 'green oil' that contribute to catalyst deactivation.[2]

Multiple suppliers provide acetylene hydrogenation catalysts with different performance characteristics and cost benefits. Each catalyst offers distinct advantages in terms of performance and cost, suitable for different applications and process requirements. When selecting a supplier for acetylene hydrogenation catalysts, it is important to consider multiple factors to ensure optimal performance, cost-effectiveness, and reliability.

A study of an 800 000 tpy plant showed that a differential in catalyst selectivity of 75% over its lifetime will result in an additional 48 million lb/yr (21 800 tpy) of ethylene – or over 2.7% of the plant's ethylene capacity.[3]

Catalysts for front-end hydrogenation have been evolving over several decades. Repsol notes significant improvements in catalyst generations, including more stable operations, reduced runaway risk, and cycles lasting over 5 - 6 years without major activity loss, with some catalysts operating for over 10 years without regeneration. Those catalysts are more expensive than the older generations, so it is important to justify their selection with an economic model that ensures gains in the produced ethylene and minimises ethylene losses (ethane production). The relationship between activity and selectivity is crucial for making an informed decision, and one of the best tools to evaluate these aspects is a supported palladium-based catalyst.

ACUs play a critical role in steam cracker plants, where significant financial investments are tied to their proper operation and the selection of appropriate catalysts. Choosing the optimal catalyst requires comparative testing of multiple catalysts to select the most suitable catalyst.

Avantium offers high throughput testing with 16 parallel reactors for evaluating acetylene hydrogenation catalysts. This article provides the results of a comparative study for Repsol of various catalyst suppliers.

Experimental

Avantium tested seven catalysts from five different suppliers under industrial front-end conditions for Repsol. The goal was to assess the catalysts' performance at three different CO levels in the feed: 400 ppm, 1000 ppm and 1400 ppm.

Reactor loading

All the catalyst samples were sent anonymised to Avantium to maintain supplier anonymity. The catalysts in this article are labelled CAT 1 to CAT 7. Avantium's Flowrence® technology uses pellets that automatically align as a string of beads in the reactor, avoiding maldistribution of gas over the catalyst bed.[4] This eliminates catalyst-bed channelling and incomplete catalyst wetting. The eight catalyst beads were loaded in the reactors, each having an internal diameter of 5.0 mm and a length of 561 mm. An inert diluent is introduced over the full length of the tube after the catalyst pellets are loaded, resulting in embedded beads. Figure 1 shows a picture of four filled (quartz) reactors, visualising the catalyst loading. In the top reactor, only catalyst beads were filled (with no diluent). The other three reactors show different diluent options: silica titania, SiC, and quartz. During these experiments, the SiC diluent of 212 - 300 μm was chosen. Additionally, a SiC diluent (1.0 - 1.4 mm) is added on the bottom and top of the reactor to make sure that the catalysts bed is within the isothermal zone (30 cm in the middle of the reactors). For a more detailed understanding of the theory supporting the use of single-pellet-string reactors, this article refers to the publications by Ortega et al[4] and Moonen et al.[5]

Reactor setup

This comparative test was carried out in a high throughput unit with 16 parallel stainless steel reactors. The reaction zone is split

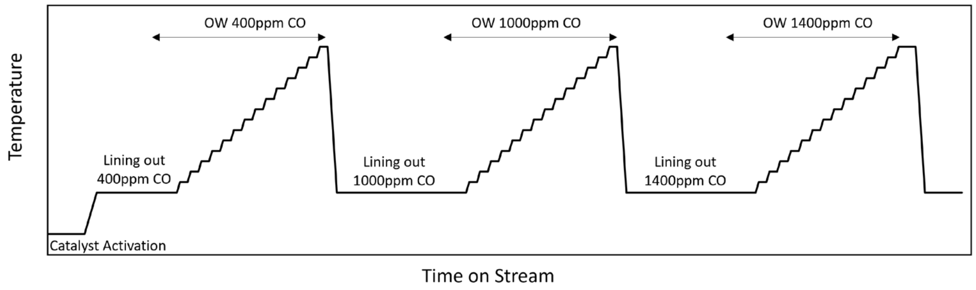

Figure 3. Schematic temperature overview during the run procedure.

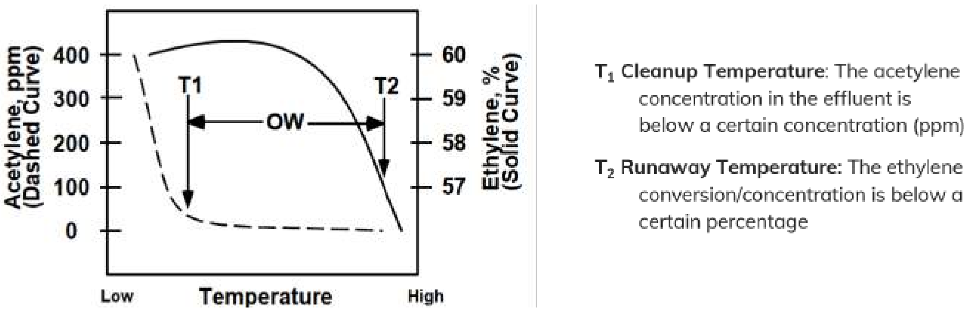

Figure 4. Operating window (OW) illustration.[7]

into four independent temperature-controlled blocks, each containing four reactors. Figure 2 illustrates a simplified schematic of the unit.

The gas feeds are measured with mass flow controllers (MFC) and are evenly distributed over the 16 parallel reactors (flow ± 0.5% RSD), using a microfluidics distribution glass chip. The microfluidics distribution glass chips are inserted in a tiny pressure module that also allows for pressure regulated within a bandwidth of ± 0.1 barg.[6] The gaseous product was analysed using an online gas chromatograph (GC). The effluent stream is diluted with nitrogen (N_2) to control the GC concentration.

Test design

The test feeds were pre-mixed in gas cylinders of 50 litres and 120 barg filling pressure. Three different feeds were tested with 400 ppm, 1000 ppm, and 1400 ppm CO concentration, mixed with H_2, CH_4, C_2H_2, and C_2H_4. Helium (3 mol%) was assessed as internal standard.

The testing programme is schemed in Figure 3. The activation procedure was discussed with each catalyst's supplier and adjusted where it was feasible. Since all the catalysts are activated in parallel, the temperature was adjusted per catalyst, while the feed composition, flowrate, and pressure remain identical for all the catalysts.

After activation, a lining-out procedure is performed. During this step, the reactors are flushed with N_2, and both temperature and pressure are stabilised at the target values corresponding to the starting conditions of the temperature scan. Once stable, the feed is introduced at the target gas hourly space velocity (GHSV).

To evaluate the activity and selectivity of catalysts used in front-end applications, the effluent gas composition is analysed using GC as the reactor temperature is gradually increased. Two key temperatures are identified during this process:

- Cleanup temperature (T_1): the temperature at which the acetylene concentration in the effluent is below 20 ppm.
- Runaway temperature (T_2): the temperature at which ethylene loss reaches 3 wt% of the ethylene in the feed, signalling the onset of significant ethylene hydrogenation.

The difference between T_2 and T_1 defines the operating window (OW) of the catalyst. A wider OW indicates a more robust catalyst against CO fluctuations, while a narrower OW may suggest thermal instability. This relationship is illustrated in Figure 4, which shows how temperature affects ethylene and acetylene concentrations and highlights the importance of OW in assessing catalyst performance.

To measure the OW, the reaction temperature is increased in steps of 2.5 - 5°C. At each step, once the desired temperature and pressure are reached, the system is allowed to stabilise for 30 - 60 minutes. The product stream composition is then measured, typically collecting three data points per reactor. After reaching T_2, the reactors are cooled back to the initial temperature under the same feed conditions (CO at ppm level). The feed is then switched, and the procedure is repeated to determine the OW for the new conditions.

Calculations

$$GHSV = \frac{m^3_{gas}}{h^1 * m^3_{cat}}$$

$$C_2H_x\ OUT\ (\%mol) = \frac{\left[C_2H_x\ OUT\left(\frac{mmol}{min}\right)\ \right]}{\left[Total\ products\ \left(\frac{mmol}{min}\right)\right]} * 100$$

$$C_2H_2\ OUT\ (ppm) = \frac{[C_2H_2\ OUT\ (mol\%)]}{100} * 1000\,000$$

$$C_2H_4\ at\ the\ reactor\ outlet\ (\%mol) = \frac{[C_2H_4\ in\ C_2\ IN\ (\%mol)] - [C_2H_4\ in\ C_2\ OUT\ (\%mol)]}{[C_2H_4\ in\ C_2\ IN\ (\%mol)]} * 100$$

Results and discussion

The performance of the seven catalysts has been evaluated in the selective hydrogenation of acetylene in front-end conditions. Figure 5 displayed the C_2H_2 content on the reactor outlet and the C_2H_4 conversion as a function of reaction temperature for the run with 400 ppm CO_2 feed. Clear differences can be observed between the conversion and selectivity's within the different catalysts. For instance, CAT 1, CAT 3, and CAT 5 reached the lower level of C_2H_2 OUT (T_1) at much lower temperatures than the remaining catalysts. In contrast, CAT 4 and CAT 6 reached the conversion targets towards C_2H_4 (and thus lower selectivity towards C_2H_6) clear at higher temperatures. It should be noted that CAT 4 has not even reached the target level for T_2 within the tested temperature range.

Lower cleanup temperatures (T_1) optimise energy consumption, while a larger OW results in longer cycles and potentially reduced costs associated with catalyst replacement. Each ACU features its own integration to ensure proper heating of the inlet and balancing between effluent-feed exchangers, outlet temperatures, and potentially steam consumption.

Lower inlet temperature requires measures to minimise contamination and procedures for unexpected events, as these factors directly impact the time needed to reach end of run (EOR) inlet temperature, ultimately limiting ethylene production.

A common operational challenge for front-end hydrogenation is the fluctuation of CO concentration in the feed. CO acts as an activity inhibitor to hydrogenation as it is adsorbed on the catalyst's active sites (the adsorption priorities are CO > acetylene >> conjugated diolefins). On conventional catalysts, when CO levels increase, a higher temperature is required to produce on-specification product. Higher selectivity can be achieved at higher CO concentrations because it functions as a favourable modifier. However, when CO concentration suddenly drops, more catalyst sites become available, and ethylene hydrogenation occurs more readily. This sudden drop can lead to temperature runaway. Therefore, evaluating catalysts at varying CO values is essential due to their impact on the stable operation of the ACU. Controlling upstream operations is particularly important when working with mixed feedstocks, such as propane, hydrocarbons, and ethane, or even circular, bio, and heavy feedstocks.

Exploring the response to CO levels, which imitate the CO swing, is a critical aspect. The rationale behind testing three levels of CO lies in preparing for temporary poisoning scenarios and ensuring catalyst stability and ethylene specification maintenance. Lower CO levels pose challenges, but higher levels may impact throughput due to ACU unit constraints.

CO influences the activity and selectivity of palladium-based catalysts as a transient poison that competes with acetylene for adsorption sites on the catalyst, thereby reducing the catalyst's activity. It is important to maintain a minimum level of CO to prevent ethylene from accessing the reaction sites. Additionally, changes in CO levels can impact the inlet temperature and the extent of acetylene hydrogenation.[7] This is evident from the test results of this run, as shown in Figure 6, which shows the OW of the different catalysts with the three different CO ppm levels. Notably, the OWs vary in length depending on the CO concentration in the feed. As previously explained and further supported by the results, higher CO concentrations require elevated T_1 and T_2 temperatures. It should be noted that for CAT 4 and CAT 6, T_2 was not reached within the tested temperature range at higher CO levels. Therefore, the actual OW for these catalysts is wider than what is shown in the figure.

Figure 7 presents the results of Figure 6 reorganised by the three feeds to make it easier to compare the catalysts performance among different CO levels.

In summary, the data in Figures 5, 6, and 7 provide a detailed comparison of the performance of different catalysts under varying CO levels. The results indicate a narrow performance gap among the catalysts, highlighting the subtle differences among them.

The primary goal is to selectively convert acetylene into ethylene. However, during this process, ethylene can also be

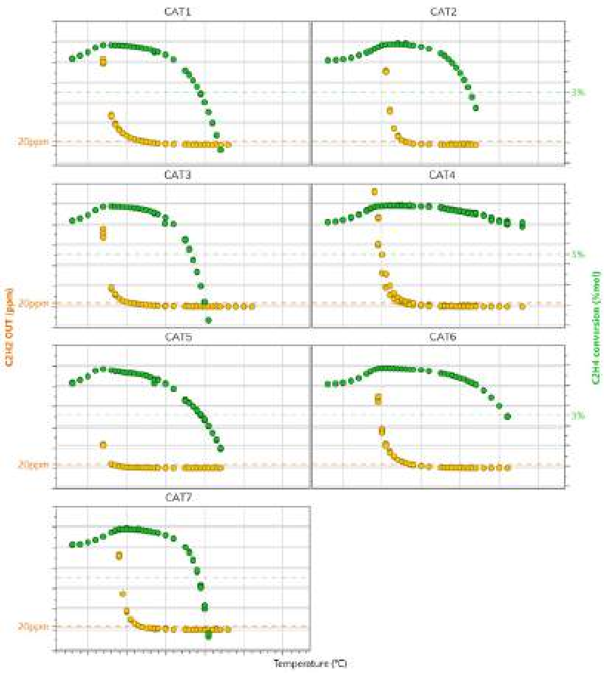

Figure 5. Operating window (OW) of the seven different catalysts with feed of 400 ppm CO.

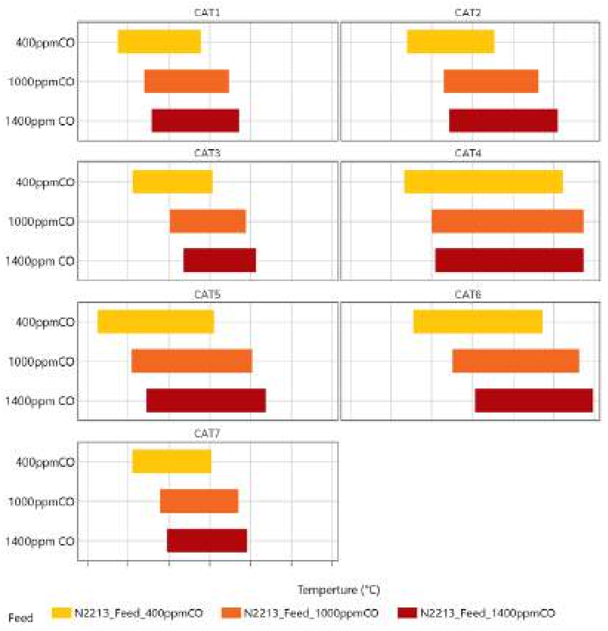

Figure 6. OW temperature ranges in comparison to different CO levels sorted by catalysts.

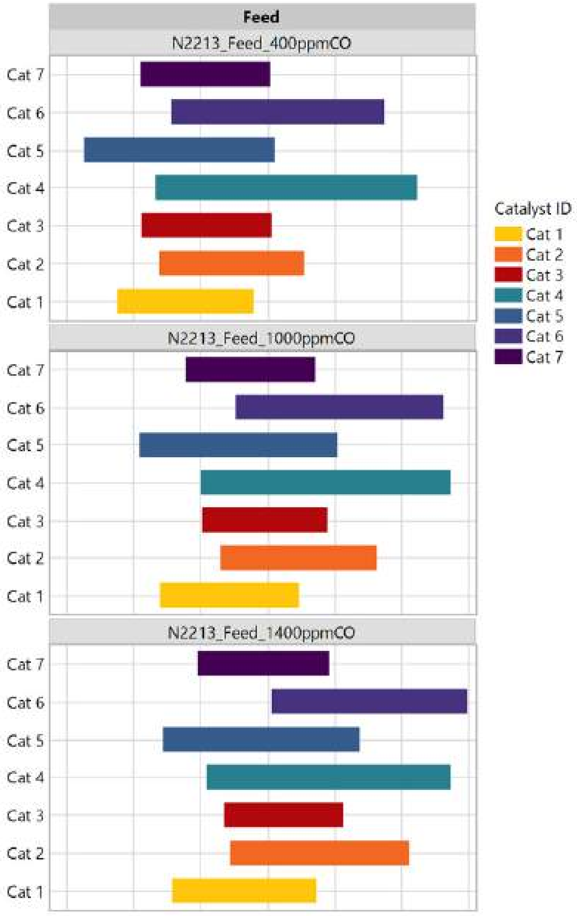

Figure 7. OW comparison of different catalysts sorted by feed with different CO levels.

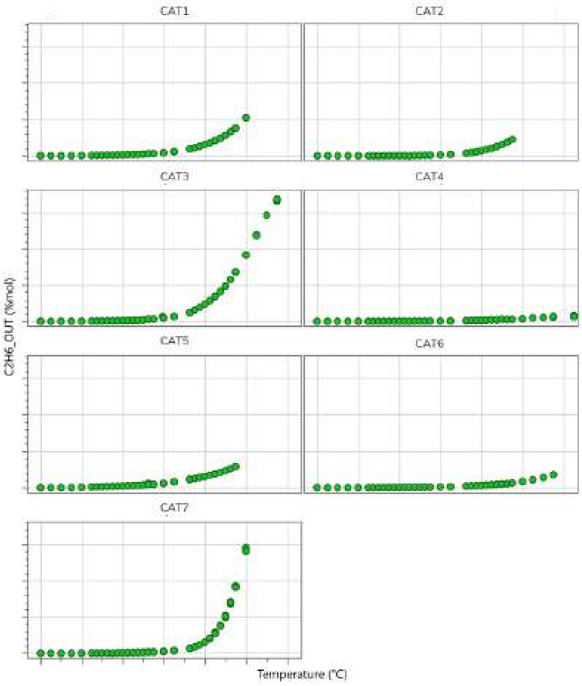

Figure 8. Ethane production of the seven different catalysts with the feed of 400 ppm CO.

hydrogenated into ethane, which reduces the selectivity for ethylene. Additionally, acetylene can undergo overhydrogenation to form ethane (C_2H_6). Ideally, a catalyst should prevent the further hydrogenation of ethylene to ethane. Figure 8 illustrates the production of ethane with the feed of 400 ppm CO, showing that different catalysts exhibit varying behaviours. Catalysts 7 and 3 produce relatively high amounts of ethane, while the others produce less. When selecting the final catalyst, the selectivity for ethane production is an important factor to consider as avoiding ethane production during acetylene hydrogenation is crucial because ethane is a less valuable product compared to ethylene.

Conclusion

The testing results underscore the importance of independent comparative testing in making informed decisions. The detailed examination of the catalysts' response to varying CO levels, their stability under temporary poisoning scenarios, and the ability to maintain ethylene specifications are crucial factors that influence the final selection.

Repsol selected the best catalyst based on the results of this study considering operational constraints and economic considerations. Through this study, Repsol has underscored the importance of independent comparative testing. Such evaluations offer a clear and impartial assessment of catalyst performance under actual operational conditions. This approach ensures that the selected catalyst is not only economically viable but also optimally suited to the plant's specific requirements, thereby enhancing overall efficiency and reducing operational constraints.

As emphasised above, economic considerations are integral to the decision-making process. The balance between activity and selectivity, as well as the importance of lower T_1 vs a larger OW, are also pivotal. For this ACU, a lower T_1 is essential due to physical limitations that prevent maximum OW from being achieved.

In summary, the economic gains associated with reduced ethane production, lower recycling needs, and energy savings due to lower inlet temperatures, underscores the financial benefits of optimal catalyst selection.

Note

- Flowrence is a registered trademark from Avantium.

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