High throughput experimentation meets chlorine chemistry

A novel high throughput unit designed for the accelerated testing of HCl oxidation catalysts under industrially relevant conditions

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Chlorine is one of the most abundant commodity chemicals in the world. About 85% of all pharmaceuticals and more than 50% of chemicals are derivatives from the chlorine value chain.[1] Two of the largest chlorine consumers are vinyl chloride synthesis (PVC monomer) and the production of isocyanates (methylenediphenyl/toluene diisocyanate [TDI/MDI]). However, the chlorination of organic compounds is always adversely affected by hydrochloric acid (HCl), which is formed as a byproduct.

While HCl is essentially recycled within the PVC value chain to a major extent, isocyanate production is flooding the market with byproduct HCl, at strong growth rates. If excess HCl cannot be recycled or valorised directly via muriatic acid, it needs to be disposed of by neutralisation or deep welling, which is expensive and detrimental to the environment. Chlorine recovery is the more desirable option from an economic point of view since it enhances the overall process efficiency and reduces the dependency on fluctuations in the chlorine market price and availability. The catalytic oxidation of HCl via the Deacon process is an attractive way to restore chlorine since it is much more energy-saving than the state-of-the-art electrochemical processes.[2]

Since the current solutions for the Deacon processes involve active but expensive Ru catalysts, the search for cheaper alternatives based on Cu or Cr is of commercial interest.[3-5] However, even if promising catalyst candidates are developed, suitable laboratory test protocols are strongly limited in the parameter space, scale, or runtime due to the corrosiveness of the chemistry. We have developed a high throughput lab-scale technology that is able to test 16 catalysts in parallel under industrially relevant conditions to address the challenges of chlorine chemistry.

Experimental

Unit design and operation

Standard laboratory equipment is usually assembled with stainless steel components. Therefore, it suffers from severe corrosion by contact with strong acidic components like HCl or chlorine, especially in a wet gas environment. Although advanced alloys with a high Ni content significantly reduce corrosion, they do not avoid it completely. A few polymer-based materials like PTFE or glass are chemically resistant but prone to breakage when operating under high temperature or pressure. The contrast of chemical versus mechanical resistance is one of the core issues that must be overcome for the high throughput testing of chlorine chemistry, especially when approaching industrially relevant testing protocols.
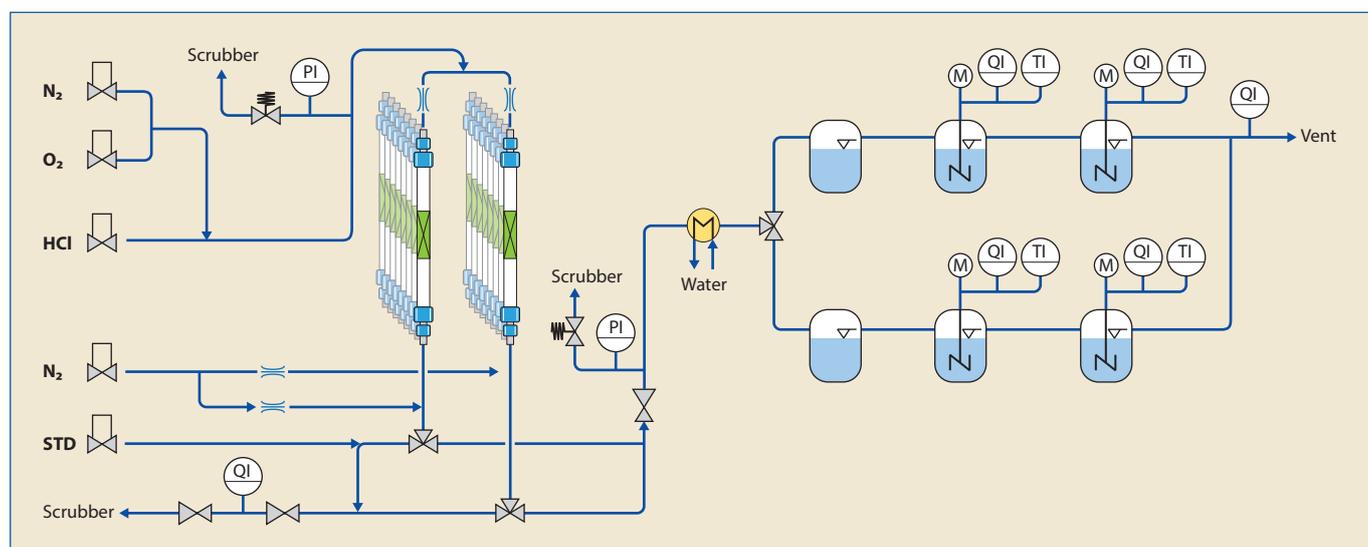
Figure 1 Simplified flow sheet of the 16-fold high throughput unit including feed section, parallel reactors, online analytics, and off-gas treatment
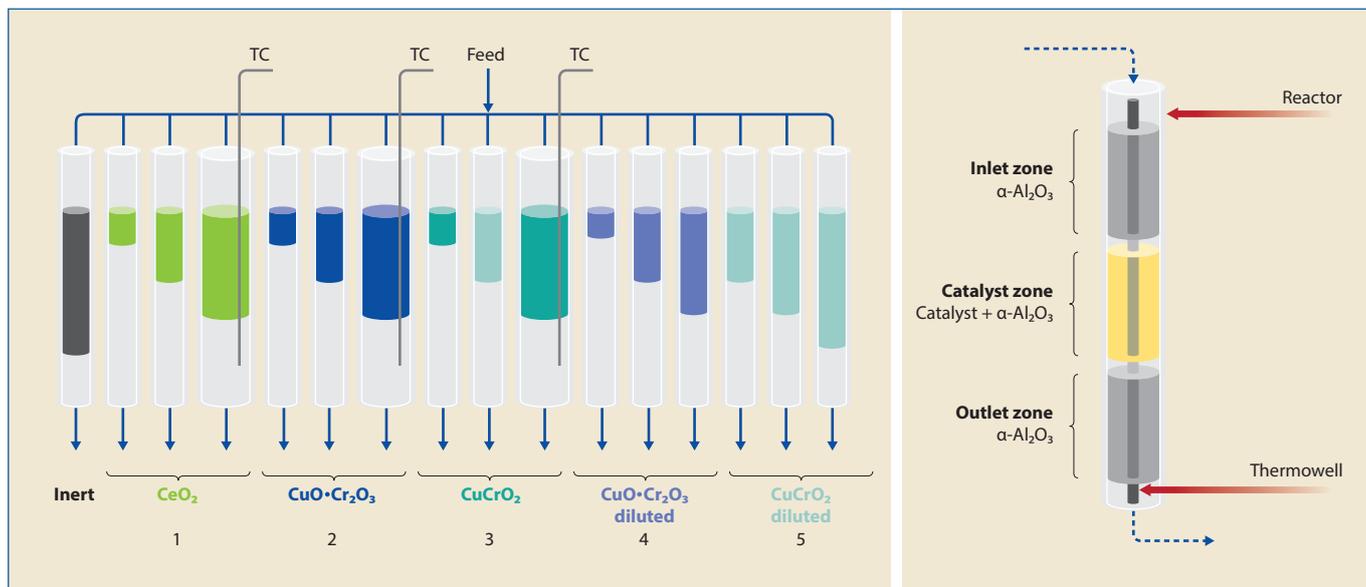
Figure 2 Reactor packing design of the 16-fold high throughput unit, catalysts (a) CeO_2 (b) $CuO \cdot Cr_2O_3$ (c) $CuCrO_2$ at different residence times and inert dilutions

Most of the state-of-the-art testing equipment operates single stage. There are only a few high throughput approaches for catalyst deactivation research. However, they work without online analytics. Furthermore, experimental programmes are often limited to mild conditions (high O_2 or N_2 dilution) and low catalyst mass or runtime.[6] We have designed a tailored 16-fold high throughput unit to accelerate the assessment of activity, selectivity, and decay for catalysts in the field of chlorine chemistry at industrially relevant conditions. It can process corrosive gases at a high hydrogen chloride intake and extended runtime that also includes off-gas treatment on a kg scale. **Figure 1** shows a simplified scheme of the 16-fold high throughput unit.

> **The contrast of chemical versus mechanical resistance is one of the core issues that must be overcome for the high throughput testing of chlorine chemistry**

HCl, pure oxygen, internal standard, and nitrogen are dosed by Coriolis and mass flow meters and distributed at equal flow into 16 channels by a controlled pressure drop. The entire upstream section is made of stainless steel parts, and the feed gas was dried to work absolutely water free. Up to 16 catalysts can be screened in parallel, operating at reaction temperatures up to 410°C and pressures of 4 barg. Reactors are made of quartz glass with a maximum catalyst volume of 1 ml (operation at +/-2K temperature deviation).

Depending on the material type, up to 2g of Deacon catalyst can be loaded per position. Online temperature profiles can be measured using a movable thermocouple placed inside a quartz thermowell. The reactor pressure is controlled by a customised membrane pressure controller. The reactor effluent can be diluted with an inert gas to prevent condensation. Subsequently, one of the channels can be selected for analysis.

The composition of the product stream is analysed by an online-FTIR developed by Gasmet Technologies. This device allows the measurement of water and HCl in a nitrogen matrix by means of robust detection even at volume per cent concentration levels above 50% HCl at a maximum sampling frequency of 1 data point/second.

This analytical method provides an efficient alternative to conventional gravimetric titration, where a poor performance differentiation between several catalysts is obtained. The entire downstream section was designed by a modular combination of polymer, alloys, and coated materials, combined in a way that temperature and elevated pressure can be run, even in a wet gas environment.

To comply with environmental standards, HCl and chlorine need to be fully neutralised. This is achieved in a multistage scrubbing unit equipped with temperature and pH control. Two CSTR trains can be run in alternating operation, each capable of removing several kilograms of chlorine, to reach a runtime of up to several months, depending on the amount of HCl fed to the unit.

From a technical point of view, experimental protocols for the Deacon reaction require, on the one hand, the right equipment; on the other hand, a lot of operational experience is also necessary to prevent severe corrosion and improve overall unit availability. The most critical corrosion issues are briefly investigated, as follows.

When processing iron or iron-rich alloys (Fe >5% w/w), the feed needs to be dried carefully since water impurities above the ppb range can form liquid clusters, resulting in severe liquid phase corrosion. This especially concerns the tube wall, where the gas velocity is zero and local cold spots may occur. Heat loss during wall contact and water condensation cannot essentially be excluded. Once a liquid phase is formed, either oxygen or HCl can diffuse inside

and accelerate the redox reaction to form iron hydroxide and thereby cause serious damage to the equipment.

However, even when alloys are operated dry, iron-containing alloys can be chlorinated or oxychlorinated when operating them at a temperature range above 160°C to 204°C, according to equations (2) and (3).[7] HCl reacts in a gas phase reaction to form a metal halide and hydrogen. Furthermore, some metal halides are volatile, especially $FeCl_3$, which sublimates at 120°C, contaminating the downstream unit equipment:

$$Fe + 2HCl \leftrightarrow FeCl_2 + H_2 \tag{2}$$

$$FeCl_2 + HCl \leftrightarrow FeCl_3 + 0.5 H_2 \tag{3}$$

Various alloy metals (such as chromium) are prone to form volatile salts that can move through the unit, depending on the surrounding conditions. Once the metal halide deposits pollute the downstream section of the unit, the major issue is their strong hygroscopic nature (deliquescence). The formation of water as a product during the Deacon reaction cannot be circumvented. If water is flowing through those substances, it will be strongly absorbed until a liquid phase is formed that consecutively acts as a corrosion hot spot. The affected part of the unit must be cleaned or replaced to remove hygroscopic deposits.

Plate design and experimental conditions
The Deacon reaction was performed using three standard catalyst systems known by the art, and it is shown in the scheme of the reactor packing design in **Figure 2**. Each single reactor packing consists of an inlet and outlet zone filled with corundum and a catalyst zone, which was placed in between, separated by glass wool layers. For a more comprehensive description, the reactors are divided into
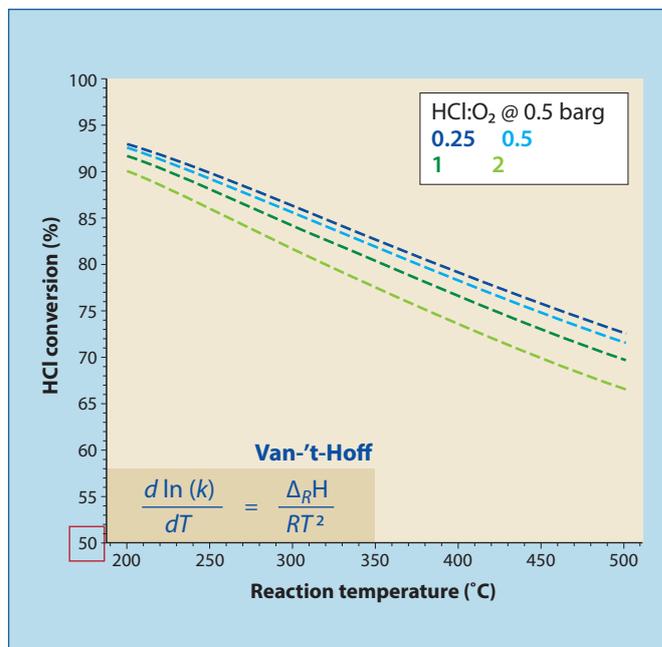

Figure 3 HCl equilibrium conversion vs reaction temperature at 0.5 barg and different HCl:O₂ molar feed ratios

triplets. Different residence times for each catalyst have been realised by filling different catalyst amounts (triplet 1, 2, 3), including one reactor per material equipped with a quartz thermowell to record online temperature profiles.

Triplets 4 and 5 represent experiments with a variation of inert dilution and duplicate positions to assess the reactor-to-reactor reproducibility. An inert position was considered to measure the feed composition. The catalysts have been screened at a reaction temperature ranging from 360°C to 410°C at an HCl:O₂ molar ratio of 0.125-2. In addition, supplementary runs at an elevated pressure of 3.5 barg have been processed.
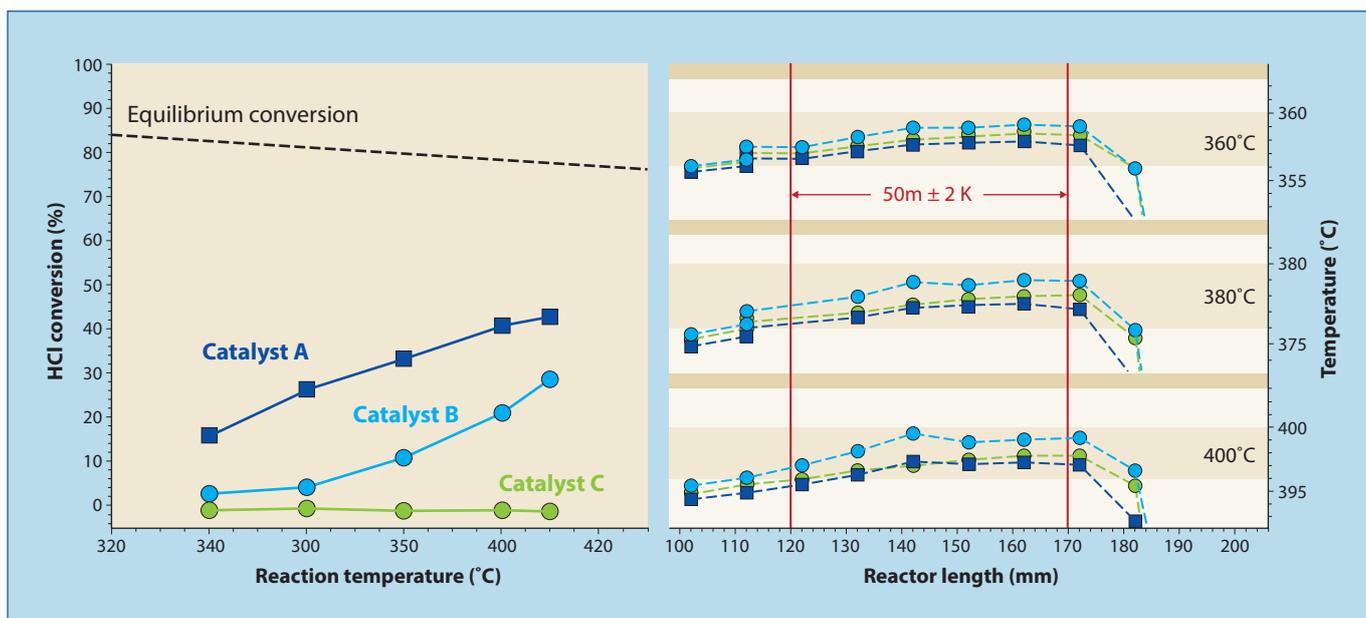
Figure 4 HCl conversion vs reaction temperature of all catalysts at 0.5 barg, HCl:O₂=0.5 mole/mole and a residence time of 600 kg*s/m³ (left), online temperature profile for reactors 4, 7, and 10 at 360°C, 380°C, and 400°C (target temperature), 0.5 barg, HCl:O₂=0.5 mole/mole and 600 kg*s/ m³, processing at a maximum temperature difference of +/-2K (right)
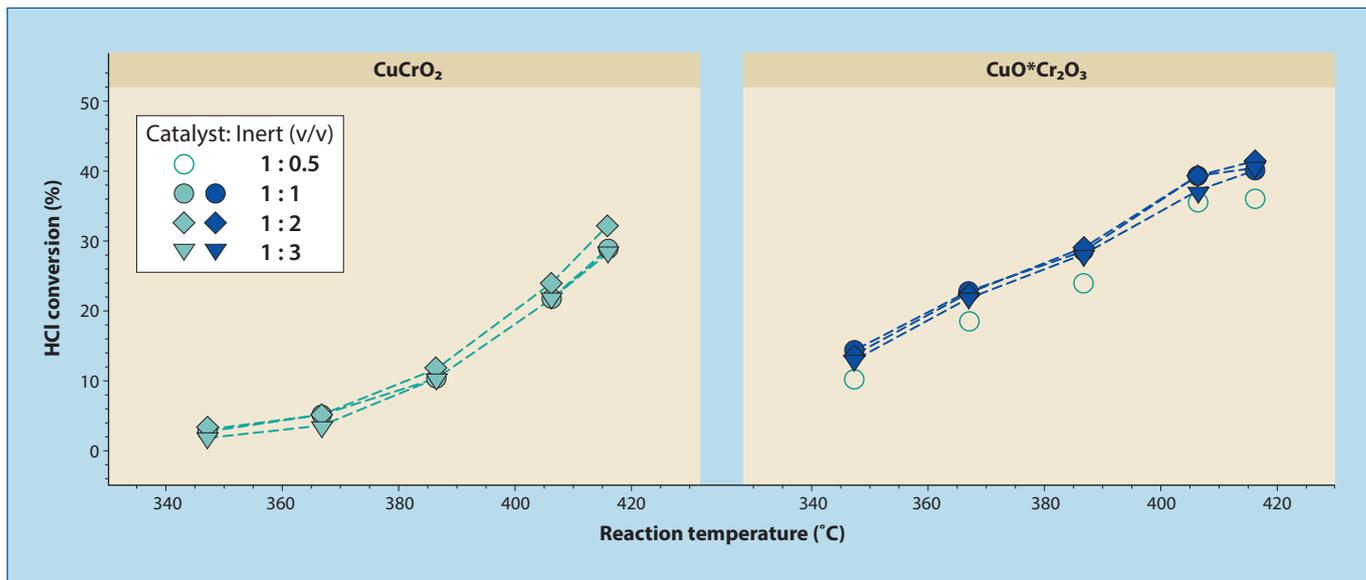
Figure 5 HCl conversion vs reaction temperature of different catalyst:inert dilution ratios at 0.5 barg, HCl:O_2 of 0.5 mole/mole and a residence time of 420 kg*s/m³

Results

The catalytic oxidation of HCl yields chlorine and water in an exothermal equilibrium limited reaction with increasing volume per mole HCl converted, Equation (1). Low reaction temperatures and elevated pressures favour high chlorine yields from a thermodynamic point of view (see **Figure 3**).

$$4\ HCl + O_2 \leftrightarrow 2\ Cl_2 + 2\ H_2O \qquad \Delta_R H^{298} = -58\ \frac{kJ}{mole_{Cl2}} \qquad (1)$$

Figure 4 (left chart) shows the activity profile of the tested materials. $CuO \cdot Cr_2O_3$ was identified being the most active catalyst, followed by $CuCrO_2$. Copper-containing catalysts typically start to be active from 350°C to 400°C. While the former material (dark blue curve) shows the highest activity at 410°C, the latter one shows a stronger increase in conversion with rising temperature, even beyond 400°C. CeO_2 slightly became active at the upper end of the observed temperature range (not shown), which agrees with the literature. However, the temperature was not raised further to protect the sensitive copper materials.

Online temperature profiles were measured indicatively for positions 4, 7, and 10 under conditions with the highest heat release rate. For all of the experiments, the temperature was kept below a maximum difference of +/- 2K, as shown in **Figure 4** (right chart). The catalyst:inert dilution was varied to ensure equal heat distribution across the catalyst bed and avoid hot spots that may lead to catalyst deactivation. The reactor of positions 5, 6, 11, 12, and 13 ($CuO \cdot Cr_2O_3$) were not equipped with a thermocouple and, therefore, the T-profiles were not measured, but the dilution ratios ranging from 1:1 to 1:3 (full symbols) show
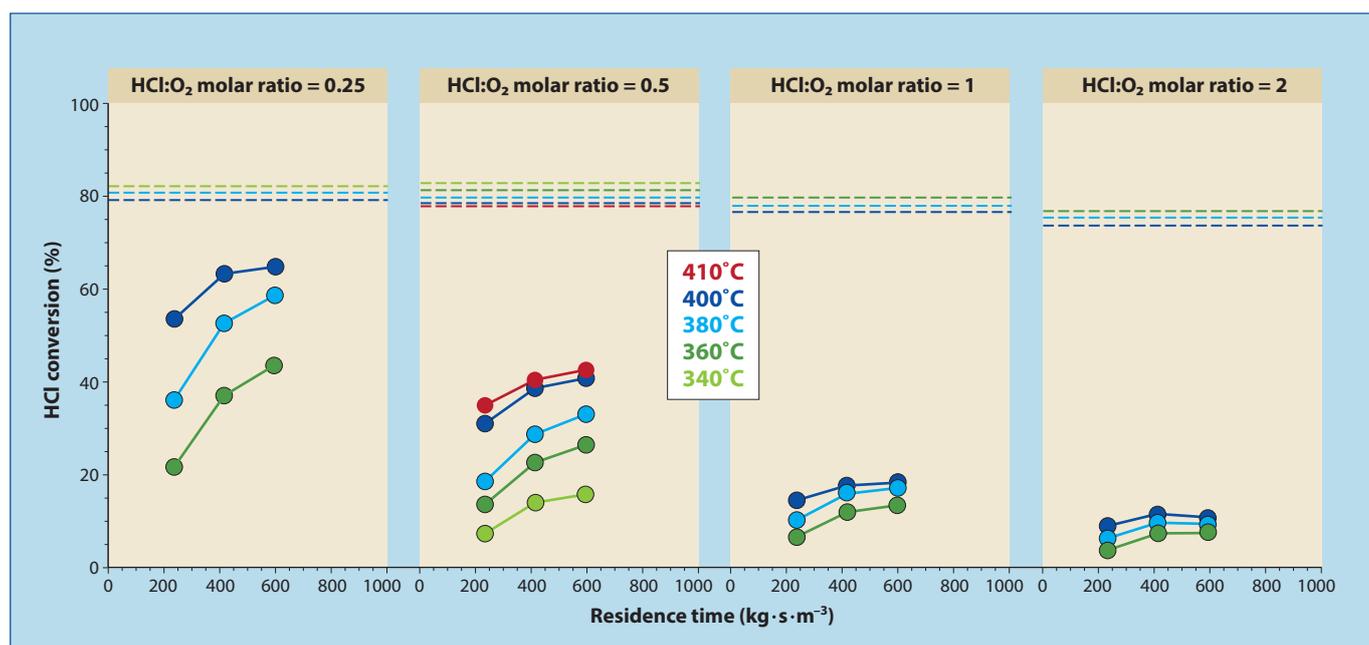
Figure 6 HCl conversion vs residence time at different reaction temperatures and molar feed ratios at 0.5 barg
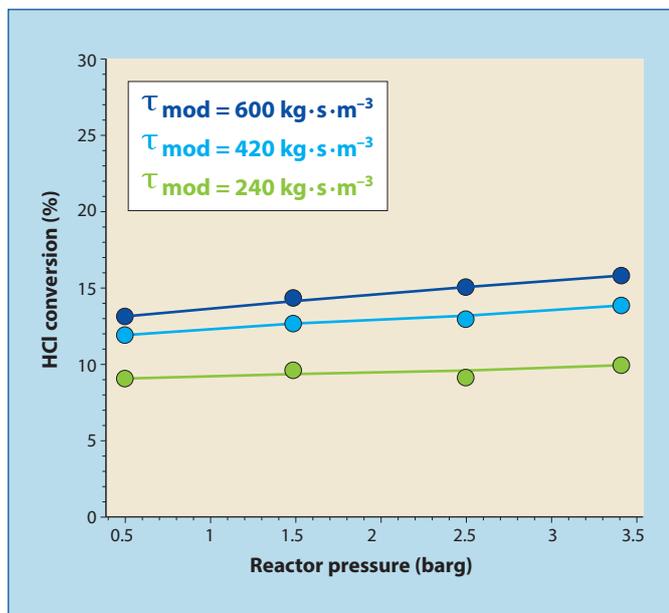
Figure 7 HCl conversion vs total pressure of CuO·Cr₂O₃ at different residence times and 380°C and HCl:O₂=0.5 mole/mole

reproducible results, suggesting those positions operate at an equal temperature profile, as shown in **Figure 5**. At the lowest dilution of 1:0.5, the HCl conversion drops for the $CuO \cdot Cr_2O_3$ (right graph, hollow symbols). It is assumed that local hot spots could not be avoided, which deactivated the catalyst. The $CuCrO_2$ was diluted from 1:1 to 1:3, which shows similar results. Based on dedicated packing protocols and exact temperature control, isothermal processing can be ensured, making this unit a powerful tool for catalyst benchmarking.

A variation of the molar feed ratio and residence time at different reaction temperatures was carried out over a broad range. The results are shown to be exemplary for the most active material $CuO \cdot Cr_2O_3$, as shown in **Figure 6**. A higher

residence time leads to higher conversion, while the results of all the experiments are still far from equilibrium (dashed lines). However, the residence time and temperature were considerably low, revealing a good catalyst performance.

Variation of the HCl:O₂ molar feed ratio revealed that higher oxygen concentration improves HCl conversion significantly. By increasing the HCl/O₂ ratio from 0.25 to 2, for example, the activity of the $CuO \cdot Cr_2O_3$ was reduced by a factor of 4 at 360°C. Total pressure varied from 0.5 to 3.5 barg at constant HCl:O₂ molar feed ratio and temperature (see **Figure 7**).

For a short residence time and thereby low conversion levels, no influence of the pressure is measurable. When approaching higher conversion at an increased residence time, higher pressure has an increasing effect on the HCl consumption. According to the reaction equation, an influence of the reverse Deacon reaction will be hampered at higher pressure levels.

The reaction temperature has a dominating effect on the catalyst performance. An increase of 20°C, from 360°C to 380°C, shows a conversion was increased by 1.5-fold. The maximum temperature tested was 410°C and only showed a minor gain in HCl conversion in comparison to 400°C. A closer look at **Figure 8** gives more insights into catalyst decay. It shows the HCl conversion versus time on stream right after a condition change.

Using the FTIR technology, a single data point could be recorded in less than five minutes, and a full turnaround of 16 reactors took a maximum of 80 minutes. This way, even small incremental changes in the effluent concentrations of short catalyst beds can be measured to describe the deactivation behaviour of Deacon catalysts.

The $CuO \cdot Cr_2O_3$ shows an initial drop in conversion at every condition, within a steeper slope at higher temperatures. Reproducibility runs after a temperature variation (black symbols) show a consistent drop in conversion, revealing the temperature as a main factor in catalyst deactivation. A
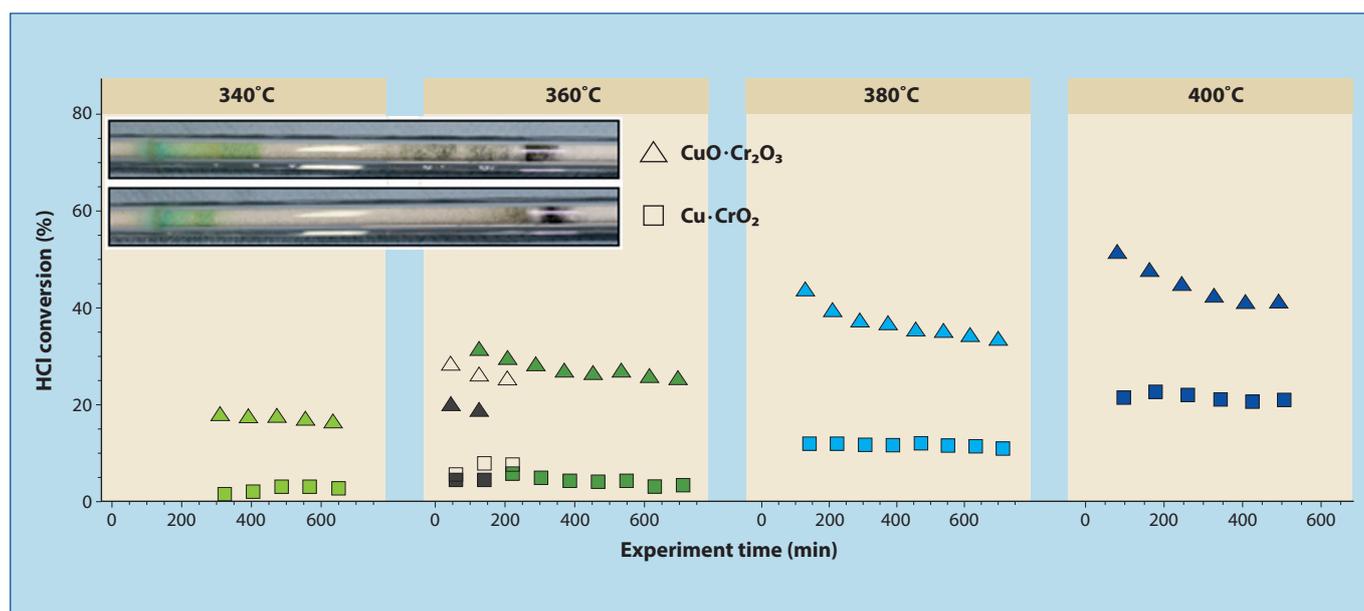
Figure 8 HCl conversion vs experiment time after conditions change for CuO·Cr₂O₃ and CuCrO₂ at 0.5 barg, HCl:O₂=0.5 mole/mole and a residence time of 600 kg*s/m³

reproducibility experiment after a feed ratio variation (hollow symbols) entails only a minor loss in activity which might also derive from temperature strain on the catalyst in consequence of the increasing runtime.

After unloading the processed catalyst, strong discolouration of the outlet inert material was found, indicating deposits of volatile copper species that escaped from the catalyst. The $CuCrO_2$ shows a significantly more stable performance after a condition change and good reproducibility. The discolouration was also less intense. Within customer projects, this unit was processed with more than 300 hours on stream and showed the excellent stability of the equipment. Mass transfer has not been investigated, which could affect the result. The mass balance was closed for all the runs.

Outlook

A high throughput unit has been developed that is suitable for chlorine chemistry, with the ability to accelerate catalyst screening at industrially relevant conditions and extended runtime. An experimental protocol was developed for the Deacon reaction, including the variation of temperature, pressure, feed ratio, and residence time in a wide parameter range.

Using a tailored, fast FTIR analysis method based on a collaboration with Gasmet Technologies allows for differentiating between a more active and stable catalyst, resulting in enhanced catalyst research. The essential concept behind this unit is transferrable to other scales in the laboratory environment and contributes to accelerated research in the field of chlorine chemistry.

References
1 Fauvarque J, *Pure & Appl. Chem.* 68 (9) 1996, 1713.
2 Asaro M, IHS Markit PEP Review *Hydrochloric Acid (HCl) Recycle to Chlorine by the Sumitomo Catalytic Oxidation Process,* December Issue (2019).
3 Iwanaga K et al., R&D Report Sumitomo Chemicals (1) www.sumitomo-chem.co.jp/english/rd/report/files/docs/20040100_p0e.pdf (last access 25.07.2022).
4 https://matthey.com/products-and-markets/pgms-and-circularity/pgm-management
5 Mondelli C, Amrute A P, Schmidt T, Pérez-Ramírez J, *Chem. Commun.* 47 2011, 7173–7175.
6 Valtchev M, Hammes M, Richter R, Höltzen H, Stöwe K, Maier W F, *Chem. Eng. Technol.* (2014) 37 No. 7, 1251-1260.
7 Ihara Y, Ohgame H, Sakiyama K, *Corros. Sci.* 21 (12) 1981, 805-817.

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