TOPICAL REVIEW

High-throughput technology for novel SO₂ oxidation catalysts

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Abstract
We review the state of the art and explain the need for better SO₂ oxidation catalysts for the production of sulfuric acid. A high-throughput technology has been developed for the study of potential catalysts in the oxidation of SO₂ to SO₃. High-throughput methods are reviewed and the problems encountered with their adaptation to the corrosive conditions of SO₂ oxidation are described. We show that while emissivity-corrected infrared thermography (ecIRT) can be used for primary screening, it is prone to errors because of the large variations in the emissivity of the catalyst surface. UV-visible (UV-Vis) spectrometry was selected instead as a reliable analysis method of monitoring the SO₂ conversion. Installing plain sugar absorbents at reactor outlets proved valuable for the detection and quantitative removal of SO₃ from the product gas before the UV-Vis analysis. We also overview some elements used for prescreening and those remaining after the screening of the first catalyst generations.

Keywords: sulfuric acid production, SO₂ oxidation catalysts, high-throughput technology, emissivity-corrected IR thermography, UV-Vis analysis

1. Introduction
With an annual volume of nearly 200 million metric tons sulfuric acid is the world’s most widely produced and one of the most important chemicals [1]. However, very few recent articles focus on the improvement of sulfuric acid catalysis, perhaps because the major manufacturing method, the double contact process, is regarded as fully developed [1]. This process has a conversion rate of above 99.5% and releases about 60% of heat (∼1300 kWh t⁻¹) [2] in the form of superheated steam. It also leaves 0.5% or more than 600 kt of unconverted SO₂, which is a ‘100 000 000 $ per year investment’ in acid rain. Meanwhile, the EU defined goals for the reduction of SO₂ emissions in their ‘Clean Air for Europe’ (CAFE) program [3] and the US tightened their corresponding standards for the first time in 40 years [4]. Therefore, new regulations for the emission of SO₂ should be expected. Below, we briefly overview the state of the art in sulfuric acid catalysis and the topics of research interest in recent years.

Almost all industrial plants include vanadium (V) in their catalysts [5, 6]. Iron-based catalysts are more stable but less active and, thus, less utilized. They can be used under high-temperature conditions (above 600°C) and with high and fluctuating feed-gas concentrations [7–10]. Niche research topics are noble metal catalysts [11–15] and systems based on activated carbon [16].

A significant effort focused on finding the mechanism of action and optimum composition of vanadium-based catalysts. In solid V₂O₅, the mechanism is based on redox cycles [17, 18], which can be described with the following reactions:

\[ \text{V}_2\text{O}_5 + \text{SO}_2 \rightleftharpoons \text{V}_2\text{O}_4 + \text{SO}_3, \]
\[ \text{V}_2\text{O}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{V}_2\text{O}_5. \]

To be suitable as a catalyst for SO₂ oxidation, a transition metal oxide has to meet several requirements. In particular, its redox cycles must be reversible and the reintegration of oxygen ions into the crystal lattice should be sufficiently fast. A precondition for this is a low Tammann temperature, \(T_{\text{Tammann}}\). At the Tammann temperature, lattice atoms possess sufficient kinetic energy for transpositions, and, thus, \(T_{\text{Tammann}}\) is about half of the melting temperature [19]. For V₂O₅,
SO₂ to O₂, with higher yields and lower SO₂ emissions. New plants could be developed without the need for an intermediate absorber. Here, the limiting conditions are defined by the quality of the end absorber. A lower ignition temperature of the process is beneficial as more superheated steam can be generated.

The low limit for reducing the reaction temperature is given by the acid dew point, which is a function of the SO₃ and H₂O concentrations. Lowering the temperature below this point leads to the condensation of sulfuric acid, resulting in damage to the equipment.

We selected the chemical composition of the oxidation catalyst as the optimization parameter in lowering the temperature of the SO₂ oxidation, aiming to find alternative elements to the commonly used vanadium. As we are dealing with an oxidation reaction, the search can be reduced to oxides and mixed oxides. Since SO₂ oxidation is exothermic and there are no parallel or sequential reactions, the heat of reaction is an attractive screening parameter, which can be deduced by emissivity-corrected infrared thermography (ecIRT).

The basic principle of ecIRT is that all chemical transformations are accompanied by a change in free enthalpy \( \Delta G = \Delta G_{\text{ad}}(\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3) = -70.8 \text{ kJ mol}^{-1} \). Therefore, the catalytic transformation on the surface of the catalyst is accompanied by heat emission. The amount of heat, and thus, the increase in temperature measured with the IR camera, is related to the conversion rate of the studied catalyst. The catalysts being studied are not black body radiators, but are gray bodies with the emissivity <1 and reflectivity >0, and the measured temperature differences are rather small. Therefore, a calibration before the measurement is mandatory, otherwise, a variation in the photon intensity would be misinterpreted as the temperature difference. The calibration is performed using a library of IR images recorded at a certain temperature step, which are compared, pixel by pixel, with the images taken during the reaction to correlate the photon intensity and reaction temperature. However, the reaction studied may change the surface structure, composition, and emissivity of the

Figure 2. Temperature dependence of the equilibrium concentration of SO₂ calculated from [35].

The concentration of inactive V⁷/V⁵⁺ compounds is plotted against the temperature for starting concentrations of \( c_0(\text{SO}_2) = 10.0\% \) and 10.9% at ambient pressure. Note that low conversion rates of over 99.9% are thermodynamically possible at reaction temperatures of 330 °C, without the need for an intermediate absorption step. This indicates the importance of developing new catalysts that can convert high concentrations of SO₂ into SO₃ at low temperatures under continuous operation conditions.

With an optimized catalyst, existing plants could process higher SO₂ concentrations, at less optimal mixing ratios of

\[ \Delta G_{\text{ad}}(\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3) = -70.8 \text{ kJ mol}^{-1} \]
catalyst, thereby distorting the ecIRT results [36]. Performing a careful six-point calibration (six different temperatures around the desired reaction temperature) allows quantifying of the temperature increase and ordering of the catalysts in a composition library [37].

Another, less obvious problem is the requirement of a similar microstructure of the studied catalysts, as different porosity, pore size, surface area, and particle size lead to different heat and mass transport phenomena, which can also affect the ecIRT readings. The most reliable results are obtained when all the materials of the catalyst library were prepared using the same synthesis and calcination procedures.

A combinatorial search for alternative catalysts requires a synthesis procedure, which is compatible with significant changes in the catalyst composition and with the use of pipetting robots. A heterogeneous catalyst should also be porous and have a homogeneous elemental distribution on the atomic scale in the bulk material. For example, a Ti–Si mixed oxide should not contain domains of titania and silica. Only then can a new catalyst composition be discovered. All these conditions are met by sol–gel synthesis procedures, which, when conducted under acidic conditions, lead to the desired porous mixed oxides. A library design software has been developed, which calculates recipes, generates pipetting lists, and transfers them to the pipetting robots [38]. A simple strategy of the catalyst design is provided by the directed evolution concept, which was applied to the development of noble-metal-free catalysts for the selective oxidation of CO in the presence of hydrogen [39]. Other successful examples are the development of hydrocarbon-selective oxidation catalysts in the presence of CO [40] and of CO-selective methanation catalysts in the presence of CO$_2$ [41]. Over the last 15 years, numerous sol–gel based recipes for a broad variety of compositions have been formulated by our group and summarized in the review [42]. In contrast to the previous studies, in this project, rapid screening of catalytic properties had to be carried out under the extremely corrosive conditions of SO$_2$ oxidation.

Here, we describe a high-throughput setup for screening arrays of mixed oxide catalysts (binary and ternary systems) under a corrosive gas atmosphere, as required in a search for alternative SO$_2$ oxidation catalysts. Table 1 lists the elements selected for the initial high-throughput screening (HTS) based on their catalytic oxidative properties, high number of reversibly interchangeable oxidation states, role as oxygen donors, and high-surface-area supports. The dopants were chosen from an in-house library of precursors adequate for the sol–gel synthesis. Base elements were applied in concentrations of 10–98% and the dopants in concentrations up to 10%.

### 2. Experimental details

#### 2.1. Catalyst preparation

The catalysts used for the data of figure 13 were prepared using the recipes described in [43] and derivatives thereof. The sol–gel recipes based on ethylene glycol or propionic acid, which were used for the data of tables 1 and 2 can be found in [42].

We have used the following chemicals: Bi$_2$O$_3$ (99.8%, CAS 1304-76-03, Alfa), diatomaceous earth (purified, CAS 68855-54-9, Aldrich), HNO$_3$ (conc., p.a., CAS 7697-37-2, VWR), H$_2$SiF$_6$ (33.5–35%, CAS 16961-83-4, Sigma-Aldrich), H$_2$SO$_4$ (conc., 65% purum, CAS 7664-93-9, Roth), KOH (99.9%, CAS 13769-43-2, Alpha Aesar), MilliQ-Water (Elga Classic UVF), NH$_3$ solution (25%, CAS 7664-41-7, Merck), NH$_4$VO$_3$ (99.9%, anhydrous, CAS 1310-58-3, Merck), KVO$_3$ (99.9%, CAS 13769-43-2, Alpha Aesar), MilliQ-Water (Elga Classic UVF), NH$_3$ solution (25%, CAS 7664-41-7, Merck), NH$_4$VO$_3$ (99.9%, anhydrous, CAS 13718-26-8, Sigma-Aldrich), Na$_2$O (99.9%, anhydrous, CAS 13718-26-8, Sigma-Aldrich), SiO$_2$ (reagent grade, Sigma-Aldrich), sodium silicate solution (10.6% Na$_2$O, 26.5%), and sulfur (99.98%, CAS 7704-34-9, Sigma-Aldrich).

#### 2.2. High-throughput screening

The layout of the catalyst libraries was obtained using the in-house software Plattenbau 1.1.3 [38]. Each catalyst was placed three times (∼10 mg per well) by hand into the wells of the slate libraries. The HTS experiments were carried out with ecIRT using a Thermosensorik IR camera equipped with a 640 × 480 PtSi-FPA detector [44].

The previously described setup [44] had to be modified for use in a corrosive gas atmosphere. The gas distribution network was replaced by Inconel tubes with Hastelloy fittings, and a new reactor made of Inconel (see figure 3) had to be developed. The gas inlet is incorporated into the reactor ring.
shows a schematic of the setup used for the screening. The gas-mixing unit consists of three Bronkhorst mass flow controllers actuated by Hi-Tec and Teo regulator valves. SO₂ (99.95%, Gerling Holz & Co.) and synthetic air (Praxair) are fed from gas cylinders. N₂ is provided by a central gas supply and is dried by a molecular sieve column (3 Å, Roth) containing a cobalt chloride moisture indicator and Drierite to suppress the formation of sulfuric acid mist.

Because of insulation effects, the temperature in the reactor is lower than the temperature indicated by the thermocouple. This thermocouple was calibrated using a second thermocouple and a disc replacing the sapphire slice. The disc had six holes to place the second thermocouple exactly above one of the six representative wells of the library filled with sand. The calibration equation was deduced as be $T_{\text{real}} (°C) = 0.85T_{\text{set}} (°C) + 0.25$ with the correlation coefficient $R^2 = 0.999$ for $T_{\text{set}} = 60–480°C$; note that for some results of this article, $T_{\text{set}}$ falls outside this temperature range.

The temperature variation $\Delta T$ was monitored for 600 s before the experiment, which was then automatically aborted if $\Delta T$ exceeded 1 °C. However, because of stabilization problems at high temperatures, this procedure was altered to the following: (i) setting the temperature ($\Delta T < 1 °C$ for 150 s), (ii) waiting for 300 s, (iii) resetting the temperature ($\Delta T < 1 °C$ for 150 s), and (iv) starting the experiment. Furthermore, the increased thermal emission of the reactor at high temperatures may overload the IR camera. To overcome this problem, a filter (Thermosensorik functionalized germanium neutral density filter with a 1% transmission in the range of 2–20 μm) was installed inside the camera (figure 4).

The measurement itself consisted of a six-point calibration (2 °C steps) in synthetic air (50 ml min⁻¹) at $T_{\text{set}} = 530 °C$ ($T_{\text{real}} \approx 450 °C$), the camera taking two images 15 min before and right before the SO₂ oxidation under otherwise identical conditions, the camera taking nine images during the reaction (5 ml of SO₂ added per min) at 1, 3, 5, 10, 30, 45, 60, 120 and 240 min, and three pictures after the reaction at 30, 60 and 180 min taken under calibrated conditions. The integration time was set to zero. A thousand frames were averaged to produce every image.

2.3. Conventional validation

Figure 5 shows a schematic of the setup used for the screening study. For clarity, the scheme is partitioned into four units.

1. The gas-mixing unit consists of three Bronkhorst mass flow controllers actuated by Hi-Tec and Teo regulator valves. SO₂ (99.95%, Gerling Holz & Co.) and synthetic air (Praxair) are fed from gas cylinders. N₂ is provided by a central gas supply and is dried by a molecular sieve column (3 Å, Roth) containing a cobalt chloride moisture indicator and Drierite to suppress the formation of sulfuric acid mist.

2. The gas distribution unit provides the gas to the reactor, bypass and UV-Vis spectrometer cuvettes. It is designed so that, at any time, a stream of dry nitrogen flows through the parts of the setup that are not in use.

3. The reactor part contains a conventional plug flow reactor used for all the validation experiments presented in this paper. The plug flow reactor consists of a quartz tube (inner diameter 5 mm, outer diameter 7 mm) placed within a heated zone. The temperature is regulated using a Juno dTron LR316 controller with the tip of a type-K thermocouple (Thermocoax 2Ablf20/350/TI/MF9F, resistant to sulfur corrosion, accuracy ±3%) placed directly in the catalyst bed. The standard deviation of the temperature during the sampling was ±0.1 °C in the range 330–450 °C. The thermocouple calibration was verified by testing it with ice and boiling water. At the outlet of each reactor, there is a glass tube filled with granulated household sugar to absorb the evolving SO₃.

4. The analytics unit consists of a PerkinElmer Lambda 25 two-beam spectrometer and an Ålborg DFUM27s mass flow, pressure and temperature meter; the spectrometer is equipped with flow-through cuvettes (Hellma), which are made of Suprasil and have an optical length of 1 cm. Both devices are connected so that they can be switched between measurements at the inlet and outlet (or...
bypass). The parameters recorded are temperature, mass flow, SO\(_2\) concentration, pressure drop of the catalyst, heat of absorption and volume of SO\(_2\) absorbed by the catalyst. The spectrometer wavelength was calibrated with a certified glass filter set (666 000, Hellma) [45]. The SO\(_2\) flow reading was verified by iodometric titration as described in [46] using a Metrohm-Titrando automated system. The linearity between the detector signal at 300.4 nm and the SO\(_2\) concentration was checked using a ‘gas mouse’ and taking at least three individual samples per data point (see figure 6). The standard deviation of the ordinate of the spectrometer was less than 0.35% of the measured value over the course of 4 days with a corresponding drift of less than 5 \(\times 10^{-4}\)%.

The oxidation of SO\(_2\) leads to a volume contraction according to the following equation:

\[
\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(s) \quad \Delta V_{\text{Factor}} = -1.5 \text{ mol/mol}_{\text{conv}}.
\]  

(1)

This contraction has to be taken into account when calculating the conversion:

\[
\text{Conv}_{\text{real}} = 1 - \frac{1 - \text{Conv}_i}{1 - \Delta V_{\text{Factor}} \times \text{Conv}_i \times \frac{V_{\text{SO}_2}}{\text{Vol}_{\text{cat}}}}.
\]  

(2)

where Conv\(_i\) is the conversion factor calculated using the UV-Vis spectrum and ignoring the volume contraction:

\[
\text{Conv}_i = 1 - \frac{\text{Detecto Signal} - 100\% \text{Conv. Value}}{0\% \text{Conv. Value} - 100\% \text{Conv. Value}}.
\]  

(3)
For validation of the catalytic activity 100.0 ± 0.3 mg of pestled catalyst was mixed with 100 mg of sand (200–500 μm particle size) and placed on a quartz wool plug in a quartz tube. The tube was inserted in the reactor and the flow rates of SO₂ and air were set to 2 and 25 ml min⁻¹, respectively. The temperature profile consisted of 1 h at room temperature, 1 h at 330 °C, 1 h at 390 °C, 1 h at 450 °C, 1 h at 390 °C, and 1 h back to room temperature. To minimize the effects of temperature and pressure on the linearity of the correlation between the detector signal and SO₂ concentration, we calibrated the spectrometer at 0 and 100% SO₂ conversion before and after each measurement. The spectrometer was operated in the time-drive mode, with an integration time of 10 s, slit width of 1 nm, ordinate maximum of 2.0 and no signal smoothing. The absorption signals obtained during the last 40 min of the temperature plateaus were averaged to obtain the mean values of the conversion factor.

3. Results and discussion

On the basis of the selection of chemical elements shown in table 1, composition-tolerant sol–gel recipes were developed or selected, and a library design was carried out with the software Plattenbau [38]. The software generated recipes for the mixed oxides in the form of pipetting lists, which were passed to the pipetting robot. The individual mixed-oxide sols were prepared in arrays of high-performance liquid chromatography vials, where the materials after gelation were dried, calcined and crushed. The thus-prepared mixed oxides were manually transferred into the wells of slate library plates. The plates were mounted in the ecIRT reactors and the heats of reactions were monitored. Best performers were selected on the basis of their relative integrated heat signals and validated individually in a conventional gas flow reactor. Conversion factors were calculated from calibrated spectroscopic signals as described in the experimental section.

3.1. Problems

Several problems were encountered during the first experiments with the high-throughput setup and the setup used for the conventional validation. The SO₃/H₂SO₄ mixture rapidly corroded the stainless steel reactor and its unheated downstream parts and polyvinyl chloride tubes (Rauclair-E) were charred by the produced sulfuric acid. This problem was solved by building a new reactor (see figure 3) made of Hastelloy and Inconel. Teflon tubes (Bola) are permeable to SO₃ at 2.4 bar (pressure drop overnight did not occur during the leak test with 5 bar of N₂ and formation of acidic droplets related to the formation of H₂SO₃ on the outside). Therefore, Teflon was replaced with Inconel wherever possible.

Even traces of moisture in the feed gas mixture led to the formation of sulfuric acid mist that interfered with the UV-Vis measurement of the product gas composition. The moisture could be traced to the N₂ gas flow and was removed by an additional absorber cartridge (mole sieve).

In the low-moisture system, freshly formed SO₃ condensed on the cold parts of the reactor. Owing to its high vapor pressure, SO₃ damaged the downstream parts and was a potential hazard for analytical equipment; therefore, SO₃ had to be removed selectively in the presence of unreacted SO₂ from the product gas. Several approaches have been studied to solve this problem. The use of H₂SO₄-impregnated quartz wool was feasible but its efficiency was low. Several carbonates showed affinity to SO₂, but at low capacities or slow kinetics. The best solution was the use of an absorber column filled with granulated sugar. Sugar is dehydrated by the SO₃, thereby completely removing it from the system. It darkens in the process, providing a visual indicator of the SO₃ absorption (see figure 7).

The ecIRT measurements suggested and conventional measurements confirmed that many of the tested substances are unstable in the sulfur-oxide-containing atmosphere and sulfatize (e.g. Cu) and/or decompose (e.g. Mo) leading to false positives or negatives. Therefore, a treatment of the libraries under reaction conditions before the catalyst screening is advantageous.

Several ideas were tested and rejected for the conventional validation. Only UV-Vis measurements proved both reliable and practical. Iodometric titration allowed us to precisely measure the conversion, but it is time consuming and difficult to automate; hence, it was only used to validate the UV-Vis results. Fourier-transform IR spectroscopy was also used but the available device had such a low dynamic range that the samples had to be diluted by a factor of 100 : 1 so as not to completely block the transmission. The method proved impractical as the cell had to be heated due to the presence of SO₃/H₂SO₄ species, and the signals from SO₂ and SO₃ were overlapping.

Because the medium to be detected is gaseous, temperature and pressure have a significant impact on the particle density in the cuvette. Thus, the calibration shown in figure 6 only proves the linearity between the detector signal and concentration but cannot be used for absolute measurements. Therefore, a two-point calibration was performed at the beginning and end of each measurement to compensate for the effects of temperature and pressure.

As the interpretation of UV-Vis data is based on the decreasing concentration of the educt and not on the direct
quantification of the product, we had to verify that the vanished SO₂ was transformed into SO₃ and not removed by leaks or absorption. This was carried out by checking the color of the sugar absorber and the generated time-dependent graph (see below). Typically, during sulfatization, the materials take up a large amount of SO₂ in a short time but also quickly ‘deactivate’. Figure 12 provides a good example of how a sulfatization diagram differs from a diagram of catalytic activity (figure 11).

3.2. IR thermography

Monitoring the heat of reaction by IR thermography requires correction of the image for the emissivity differences at reaction temperature, which is achieved by collecting the library image before or after the catalytic reaction. Subtraction of this image from that obtained under reaction conditions yields temperature differences, which can be associated with the heat of reaction. To quantify this temperature difference, the camera is calibrated at several temperatures around the reaction temperature before the reaction. Individual spots in the image were automatically identified by the software and the spot temperature was determined by averaging over the spot area.

The ecIRT system responds to the introduction of SO₂ with a steep temperature increase corresponding to the SO₂ absorption, which is also seen during the conventional validation wherein the temperature can overshoot by up to 30 °C. After 30–60 min, the conditions stabilize and the spots that heat up during the first few minutes cool down to the surrounding temperature. Figures 8 and 9 are typical ecIRT images used for demonstration, and figure 10 is the image used for figure 13. The image of figure 8 was taken during the reaction, and that of figure 9 after the SO₂ feed was switched off. Several effects can be explained by comparing these two pictures. The red arrows mark the spots whose ‘activity’ declines after stopping the SO₂ feed, as expected for a catalyst. The black arrows indicate a spot that appears ‘active’ even without the SO₂ flow and, therefore, is likely a false positive. The green arrow points to a spot that cannot be quantified as it falls outside the calibrated range. This may happen because the spot changed its structure/composition during the reaction and its gray body radiation spectrum changed accordingly. The suitability of the materials falling into the three aforementioned categories needs to be verified using the conventional plugged flow reactor setup. However, more than ¾ of the other materials showing no activity at all can be sorted out immediately. A problem showing up in several measurements was the difficulty of comparing catalysts prepared via different synthesis routes.

3.3. Conventional validation

Measurements in the plug flow reactor were performed to assess the high-throughput setup. The data quality achieved with the UV-Vis setup is very high. Not every data point shown in figure 13 was recorded several times. Figure 11 shows a conventional experiment (catalyst No. 3 in figure 13) including a validation run with fresh catalyst as a reproducibility example. The temperature and conversion are plotted versus time. It can be seen that the conversion correlates well with the temperature ramp. Contrary to figure 11, the ‘conversion’ peaks at the beginning of each heating step in figure 12. After 2 h of measurement, at 390 °C, the uptake of SO₂ reaches its maximum, whereas after 4 h, when the temperature returns to 390 °C, no further uptake is observed, indicating saturation of the material. This behavior can be unambiguously associated with sulfatization reactions.

Two measurements per day can be carried out using the described procedure. As the validation is the bottleneck of our
screening process, we aim to triplicate the throughput with the launch of a 10-fold parallel reactor.

3.4. Comparability of ecIRT screening and conventional results

Figure 13 compares the ecIRT results of figure 10 in `per pixel’ with the conversion measured by the conventional validation. Per pixel is an arbitrary unit used by the camera software to quantify the heat emission (which is proportional to the heat of reaction and, therefore, the conversion) detected by the cluster of localized pixels of the IR detector associated with an individual catalyst well. It can be seen that ecIRT allows the clear identification of the leading candidates of the catalyst library. The correlation of heat of reaction from screening with observed conversion from conventional validation is best with the more active catalysts and drops with lower activity. For catalysts 8 and particularly 9 the per pixel values are much higher than expected from the conventional validation. As this result was reproduced over consecutive measurements, we assume that a reversible emissivity change occurs upon adsorption. Considering the results discussed in sections 3.2 and 3.4, we conclude that ecIRT is a valuable tool for the rapid screening of a large and diverse parameter space.

Since up to 206 catalysts can be screened per measurement, about \( \frac{1}{3} \) of them can be sorted out immediately and the leading candidates be identified. As to comparing the selected catalysts, the deviation of the mean values is too high, and numerous interfering effects make such a comparison unreliable. Therefore, the ecIRT measurements should be supplemented by conventional validation.

3.5. Confinement of the parameter space

Over the course of this as yet unfinished study more than 1000 samples of the type \( A_a B_b O_z \) and \( A_a B_b C_c O_z \) have been screened using the high-throughput setup, and over 250 materials have been tested in the plugged flow reactor. This narrowed the composition space for a further search for better catalysts. Several candidate elements were excluded from table 1 (as shown in table 2) because of low activity (Mn), volatility under reaction conditions (Mo), instability to the synthesis conditions (W) or generation of strong noise in the IR images (Cu).

4. Conclusions

We have developed and tested the workflows for the high-throughput and conventional validation of \( \text{SO}_2 \) oxidation catalysts for the synthesis of sulfuric acid. Several problems related to the specific demands of this project have been solved. It was shown that high-throughput methods are valuable tools in the search for better materials or catalysts, particularly for the rapid screening of a large number of samples. We also found that ecIRT cannot be used to reliably evaluate the differences between samples; while this technique can be used as a prescreening tool, conventional validation should be employed for the final evaluation. A wide composition space has been screened over the course of this study, and we hope that our ongoing measurements will further narrow the parameter space for potential \( \text{SO}_2 \) oxidation catalysts. In particular, we expect to develop new efficient catalysts based on the elements listed in table 2.
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