Activity and Deactivation of Molten Salt Catalyst
During SO$_2$ Oxidation and SO$_2$ Removal from flue gases.

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Abstract
Catalytic activity of commercial SO$_2$ oxidation catalysts have been measured in a
simulated flue gas from coal fired power plants, both with and without the typical water
vapour content. This shows that usual sulfuric acid catalysts are not affected by the the
water content, but a specially adapted catalyst with a different pore size is. An ESR
investigation of the catalyst suggests, that it deactivates due to precipitation of a V(III)
compound and not V(IV) as usual for sulfuric acid catalysts.

Introduction
The industrial catalyst for SO$_2$ oxidation, which is the key step in the production of
sulfuric acid can, at operating conditions, be described by the melt-gas system
M$_2$SO$_4$/V$_2$O$_5$/SO$_2$/O$_2$/SO$_3$/N$_2$, where M = Na, K or Cs or mixtures of these. While the
catalyst works well at rather high temperatures (> ca. 440 °C), it deactivates below this
temperature and thus limits the degree of conversion for the exothermic oxidation. This
results in SO$_2$ emission to the environment. Therefore, but also from a process design
point of view, an active 'low temperature' catalyst has been needed for many years, but
so far it has not appeared.

This need has been further increased during the last decade where attention has
been drawn to abatement of industrial flue gasses, including those from coal fired power
plants. Several methods exist to remove SO$_2$ from off-gases, but all of them, except con­
verting it into sulfuric acid, creates new types of waste (e.g. gypsum). The catalyst used
for oxidizing SO₂ in flue gasses into sulfuric acid is essentially identical to the usual catalyst used for production of sulfuric acid. However, due to a lower SO₂ concentration in flue gasses, the deactivation occurs at a slightly lower temperature. It is evident, that an active 'low temperature' catalyst is highly desirable for this purpose.

The operation conditions of the catalyst during flue gas purification is very different from the ones in sulfuric acid production. Not only the SO₂ concentration is much lower, but the 'wet' gas probably influences the chemical composition of the catalyst too, by transforming pyrosulfate into hydrogensulfate:

\[ S_2O_7^{2-} + H_2O \rightleftharpoons 2HSO_4^- \]  \[ 1 \]

The flue gas from a typical coal fired power plant is approximately 0.2% SO₂, 4% O₂, 7% H₂O, 14% CO₂ and 75% N₂.

The results presented here are a part of our continuous investigation of the sulfuric acid catalyst and its chemistry by a multiinstrumental research strategy - see e.g. ref. 1-6. By using both real industrial catalysts and well defined model melts and comparing the results, we can increase the knowledge of the catalytic system. Here we have measured the activity and recorded ESR spectra of commercial catalysts in flue gas with and without water vapor in order to investigate the influence of this component. We have also isolated compounds from catalyst model melts in the two feed gasses at the conditions of industrial operation.

**Experimental**

The flue gas was premixed in gas bottles using dry SO₂, O₂, CO₂ and N₂ to the desired composition. Wetting of gasses was done by bobbling the gas through water containing flasks heated to the appropriate temperature, e.g. 40 °C for a water content of 7% (saturation). The SO₂ concentration was monitored by UV spectrophotometry using a gas cuvette with an optical path of 50 mm. The concentration of CO₂, O₂ and N₂ was found by gas chromatography (Supelco Chromosorb 102 and Molecular Sieve 5A). The H₂O concentration was measured by a Jenway 5075 Humidity meter.

For the activity measurements and compound isolation the gas was led to a
molten salt reactor cell of Pyrex as shown in Figure 1. The crushed catalyst or model melt is supported by the porous glass filter disk through which the gas bobbles. The conversion of \( \text{SO}_2 \) was monitored spectrophotometrically (on line) and was always below 20%. The reactor cell was placed in a double walled kanthal wire wound quartz furnace. This setup allowed direct visual inspection of the crystal formation at high temperature.

For the ESR measurements, the gas was led to a quartz cell as shown in Figure 2. This cell fits into a Bruker ER4114HT high temperature X-band cavity mounted in a slightly modified JEOL JES-ME-1X instrument. The temperature was measured by a non-magnetic chromel-constantan thermocouple positioned on top of the catalyst.

The industrial catalyst samples were delivered by the manufacturer, Haldor Topsøe A/S, Denmark. Chemicals for the model melts were commercial grade \( \text{V}_2\text{O}_5 \) (Cerac, > 99.9%) and alkali pyrosulfates made by thermal decomposition of the corresponding alkali peroxodisulfate (> 99.8% by gravimetric analysis)\(^1\).

**Results and Discussion**

**Catalyst Activity**

The activity of three industrial catalysts with the approximate compositions given in Table 1 has been measured in the temperature range around 350 - 500 °C. All catalysts have a total vanadium content of around 6% \( \text{V}_2\text{O}_5 \) in the solid support of kieselguhr. VK38 is the widespread K and Na promoted type used for conversion of gasses with high \( \text{SO}_2 \) content (~10%), i.e. in sulfuric acid plants. VK/WSA is used for flue gas conversion with low \( \text{SO}_2 \) content (~0.2%) and it has the same chemical composition as VK38 but a different poresize of the solid support. VK58 has a modified chemical composition - it includes Cs in addition to K and Na as promoter. It is considered to have a higher low-temperature activity. The measured catalytic activity of these catalysts in 'dry' and 'wet' flue gasses are displayed in Figure 3 and 4, respectively. In both type of gasses all catalysts show a marked decrease in the activity at a certain temperature - the break point temperature \( T_b \) as given in Table 1. The trend in \( T_b \) for the different catalysts are in accordance with the industrial experience. However, it seems curious that
VK/WSA in 'dry' gas deactivates at a higher temperature that both VK38 and VK58. None of the catalysts meet the desire of a $T_b$ of 350 °C or lower. Therefore we have decided to undertake investigations that could explain the catalyst deactivation in flue gasses.

In situ ESR-spectroscopy

Series of ESR-spectra of the three catalysts converting both 'dry' and 'wet' flue gasses have been measured in the approximate temperature range 450 - 300 °C. The spectra obtained on VK/WSA are shown in Figure 5A and 5B for 'dry' and 'wet' flue gas, respectively. At higher temperatures the spectra shows a broad rather weak unresolved line which is attributed to polymer (or dimer) V(IV)-complexes in solution. By lowering of the temperature in the 'dry' gas a sharp almost isotropic line appears around 439 °C, i.e. at the temperature of deactivation as observed in Figure 3. By lowering the temperature further, a g-value of 1.972 can be found for the line. The spectrum is identical to the ESR-spectrum of the compound $K_4(VO)_3(SO_4)_5$ which has been isolated from model melts and earlier been shown - by in situ ESR spectroscopy - to deactivate VK38 in sulfuric acid synthesis gas. In 'wet' flue gas the ESR-spectrum shows the broad line at higher temperatures too, but no sharp isotropic line is observed at lower temperatures, not even far below the breakpoint temperature of 386 °C (Table 1). A double integration of the spectra shows that the V(IV) amount increases with decreasing temperature down to ca. 380 °C. Below this temperature, the V(IV) amount decreases. This behavior indicates that the catalyst is deactivated by ESR silent V(III) compounds: below $T_b$ vanadium is removed from the liquid phase into solid V(III) compounds, which causes the decrease of the V(IV) concentration. Further work is in progress to identify this V(III) compound by isolating it from a model melt at the same conditions in the reactor cell. Earlier the V(III) compound $KV(SO_4)_2$ has been isolated and characterized from similar catalyst melts, but at much higher SO$_2$ partial pressure. It is interesting that in this 'wet' gas both VK38, which is chemical identical to VK/WSA, and VK58 deactivates due to precipitation of the V(IV) compound $K_4(VO)_3(SO_4)_5$. This indicates that
the support has an important role for the nucleation of the compounds.

**Key words:** ESR-spectroscopy, vanadium compounds, wet sulfuric acid process.

**References**

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**Table 1:** Temperature of the Activity Drop in Industrial Molten Salt Catalysts and Compound Formation in Catalyst Model Melts.

| Industrial Catalyst | Composition of model melt (molar ratio) | \(T_b\) (°C) \(^a\) | Colour of Crystalline Precipitate |
|---------------------|----------------------------------------|-----------------|---------------------------------|
| VK38 \(^b\)         | K/Na/V = 3/0.8/1                        | 421             |                                |
| VK58 \(^b\)         | K/Ca/Na/V = 3/1/0.25/1                  | 380             |                                |
| VK/WSA \(^b\)       | K/Na/V = 3/0.8/1                        | 436             |                                |
| VK38 \(^c\)         | K/Na/V = 3/0.8/1                        | 420             | green and pale blue crystals   |
| VK58 \(^c\)         | K/Ca/Na/V = 3/1/0.25/1                  | 381             | bright blue crystals           |
| VK/WSA \(^c\)       | K/Na/V = 3/0.8/1                        | 386             | green and pale blue crystals   |

\(^a\) \(T_b\) is the temperature at which the break point in the Arrhenius plots and the compound precipitation occur simultaneously.

\(^b\) Feed gas: 0.2% \(\text{SO}_2\), 4.5% \(\text{O}_2\), 15.1% \(\text{CO}_2\) and 80.2% \(\text{N}_2\).

\(^c\) Feed gas: 0.2% \(\text{SO}_2\), 4% \(\text{O}_2\), 7% \(\text{H}_2\text{O}\), 14% \(\text{CO}_2\) and 75% \(\text{N}_2\).
Figure 2. ESR-reactor cell. (a) Thermocouple inlet, (b) Gas outlet, (c) Teflon stopper, (d) Gas inlet, (e) Catalyst bed.

Figure 1. Molten-salt reactor cell. (a) Catalyst melt, (b) sintered glass-filter disk, (c) bottom ampule for filtrate collection. Arrows indicate direction of flow during catalyst operation. The flow direction is reversed for filtering the melts and isolating the crystalline precipitates.
Figure 3: Arrhenius plots of the industrial catalysts in a dry flue gas consisting of 0.2% SO₂, 4.5% O₂, 1.1% CO₂ and 80.2% N₂.

Figure 4: Arrhenius plots of the catalysts in ‘wet’ flue gas, e.g. 0.2% SO₂, 4.0% O₂, 7.0% H₂O, 14.1% CO₂ and 74.8% N₂.
Figure 5: ESR spectra of WK/WSA catalyst at various temperatures in (A) 0.2% SO$_2$, 4.5% O$_2$, 15.1% CO$_2$ and 80.2% N$_2$ or (B) 0.2% SO$_2$, 4% O$_2$, 7% H$_2$O, 14% CO$_2$ and 75% N$_2$. 