

Au-catalysts in the Purification of TRS Emissions

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I Introduction

Total Reduced Sulfur (TRS) compounds are a group of typical emissions of the pulp and paper mills. These compounds include very malodorous compounds, such as H₂S, methyl mercaptan (MM) and dimethyl disulphide (DMDS) and they cause annoyance to the surrounding areas even if they were very diluted and cause no direct harm to the nature or the human health at these concentrations.

The TRS emissions may be concentrated or diluted. The concentrated emissions can be incinerated in a lime kiln and the SO₂ formed may be further used in sodium bisulfite (NaHSO₃) production. Concentrated emissions may also be incinerated in a recovery boiler or in a separate incinerator. The oxidation of concentrated sulphur-containing volatile organic compounds (S-VOCs) increases the energy-efficiency of the pulping process unit where they are treated. The problem arises when diluted TRS emissions are considered. They are emitted from several sites in a process and very often they cannot be easily controlled by process optimization. Due to very low odour threshold limits, the requirements for the emission abatement efficiency are very high. Furthermore, the explosion limits of these gases should be taken into account, which means that for example mixing of concentrated and diluted emissions and simultaneous treatment cause substantial explosion hazard. Therefore, these two emission types should be treated separately.¹

The abatement of diluted TRS emissions can be carried out efficiently and economically by means of catalytic oxidation. However, application of a catalytic process to this kind of field of operation is not straightforward due to difficult process conditions for the catalyst and the construction materials of the abatement unit. Currently, the greatest problem in industrial scale applications of catalytic oxidation of TRS compounds is that traditionally used noble metal catalysts, such as platinum, are too active in oxidation and cause formation of SO₃. SO₃ is reported to be formed from SO₂ over Pt at temperatures of 250–600°C depending on the support material (Koutsopoulos et al. 2006). SO₃ is quite unstable and reacts quickly with water vapour present in a gas stream to finally end up in the formation of sulphuric acid. Corrosion problems can be avoided in a certain level by keeping the inner surfaces of the oxidation system above the dew point temperature of sulphuric acid. Preferably, this could be done by tailoring the catalysts and avoiding the formation of SO₃.

In TRS emission abatement, sulphur-containing compounds and oxidation products may cause problems also with long-term durability of the catalysts. Oxidation products can form sulphates with the supporting metal oxides or very stable surface metal sulphites with the active metal. Sulphur can also be deposited on the catalyst via decomposition of H₂S and it will then inhibit the chemisorption of small molecules such as H₂, CO, NO, C₂H₃ etc. However, sulphur poisoning is reversible and it is dependent on the temperature. In fact, among the transition and noble metals, Au exhibits the lowest reactivity towards sulphur and may therefore offer a good solution for the catalytic oxidation of TRS emissions.

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The new ways of operation, novel catalysts and durable construction materials are essential in successful application of the catalytic oxidation process. New interesting possibilities are arising from the application of microwave heating, combined adsorption and oxidation abilities of certain catalytically active materials, the possibilities of low or high operation temperature which will determine the needs for e.g. construction materials. (Ojala et al., 2005, Ojala, 2005, Kucherov et al. 2006, Pitkäaho et al. 2007)

2 Objectives of the research

The objective of the research is to optimize and develop a reverse-flow catalytic incineration process to achieve good and economic abatement efficiency of TRS emissions. Efforts in this research are focused on the development of novel and innovative Au-based catalysts and on testing them in MM and DMDS oxidation.

3 Results

The catalysts were prepared either from HAuCl_4 or Au-acetate by means of deposition-precipitation. The catalysts were supported on pulverized or pelletized Al_2O_3 powder and a knitted (Kynol TM) activated carbon matt. After preparation, the catalysts were washed with deionized water and calcined at 200°C for 2 h. The specific surface areas, pore volumes and Au-loadings are presented in Table 1.

Table 1 Characteristics of the catalysts (n.d. not determined).

Catalyst	Form	BET [m^2g^{-1}]	Specific pore volume [cm^3g^{-1}]	Au loading [wt-%] before	Au loading after
Au/C	Powder			1.9	1.4
2Au/Al	Powder	330	1.2	1.4	1.1
2.7Au/AIP	Pellet	360	0.39	0.06	0.06
3.6Au/AIP	Pellet	380	0.42	0.5	0.5
Au/C2	Knitted	1680	n.d.	n.d.	2.1

The experiments were carried out in a tubular flow reactor. The feeding of the liquid model compound (DMDS) was carried out by using a syringe pump and an evaporator. The gas flows (MM, air) were controlled by mass flow controllers.

The concentration of the test compounds was $\sim 1100 \text{ mg m}^{-3}$, whereas the temperature and GHSV varied depending on the experiment.

3.1 Catalytic oxidation of MM and DMDS

Activated carbon used as a support material allows very high adsorption of the reacting MM as well as the oxidation products. During the test the catalyst was heated 3°C min^{-1} to temperatures of 59, 100, 150, 200 and 250°C . At the end, the feeding of MM was stopped and the catalyst was heated to 350°C in order to follow desorption of the adsorbed compounds. During the heating, the first signal of SO_2 was seen at 100°C and it increased at 250°C , but the mass balance was never fulfilled during the experiment. The GHSV used was $\sim 118200 \text{ h}^{-1}$.

The 2Au/Al catalyst adsorbed MM at the beginning of the experiment, but at the same time, formation of DMDS as a partial oxidation product of MM was observed. SO_2 was observed already below 100°C , and the complete conversion of MM was achieved at 150°C . The DMDS by-product was completely oxidized at 250°C . Again, the mass balance of sulphur was not fulfilled ($\text{GHSV} > 59\,000\text{ h}^{-1}$). In MM oxidation, the tested catalyst seems to be more active than the commercial noble metal catalyst.

Further tests were carried out with DMDS, since it is a partial oxidation product of MM and more difficult to oxidize completely. The GHSV in further experiments was $\sim 31\,500\text{ h}^{-1}$, the catalyst was heated from room temperature with the heating rate of 5°C min^{-1} until the complete conversion of DMDS. The experiments were carried out over a pelletized or knitted catalyst. The complete conversion of DMDS over both pelletized catalysts 2.7Au/AIP and 3.6Au/AIP were achieved at around 500°C . The oxidation of DMDS over both the catalysts started already at a very low temperature, according to the formation of SO_2 . Before complete conversion of DMDS, a slight formation of dimethylsulphide (DMS) was observed. Au-catalysts, supported on the materials that allow good low-temperature adsorption (activated carbon), are very attractive catalysts in a microwave (MW) assisted abatement process. Gold is the compound that can adsorb MW energy very efficiently and therefore it could allow the oxidation of MM and DMDS. This gives an interesting opportunity also in terms of industrial applications where it is possible to use highly durable materials towards acid corrosion that are not tolerant to high temperatures. However, the mechanism of oxidation and source of oxygen should be verified to be able to forecast the application possibilities better. Further investigations are also needed in the adsorption-desorption behaviour of the reactants and products.

In general, the results presented here show very interesting application possibilities of Au-catalysts towards the abatement of TRS emissions. However, longer term durability as well as deactivation-regeneration possibilities should be further studied before forecasting industrial-scale applications.

4 Relevance of the research

Catalytic incineration can be used in several applications to reduce organic greenhouse gases such as different VOCs. The successful application requires the development and tailoring of the catalytic materials case-by-case. There is a vast amount of research information on catalyst development in general, but there are only a few groups in the world that specialize on VOC abatement. However, an increasing interest towards VOC abatement catalysis can be foreseen.

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Reference to this article:

Ojala S., Mikkola J.-P. and Keiski R. L. (2010) Au-catalysts in the Purification of TRS Emissions.

In: Pongrácz E., Hyvärinen M., Pitkäaho S. and Keiski R. L. (eds.) Clean air research at the University of Oulu. Proceeding of the SkyPro conference, June 3rd, 2010, University of Oulu, Finland.

Kalevaprint, Oulu, ISBN 978-951-42-6199-2. pp.50-53.



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