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Flue Gas Cleaning With Alternative Processes and Reaction Media

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With the explosive increase in research and investments in green chemistry processes, combined with the increasing concern for human impact on the environment, follows a natural interest for using new innovative technologies for treating classic well known pollution problems such as flue gas cleaning. In this contribution we present some of the ideas evolved from our laboratories within the last years aimed towards flue gas cleaning. Generally, the technologies use ionic media, likely combined with some sort of transition metal catalysts. The goal is to develop novel so-called “waste-to-product” technologies.

An inspiration for waste-to-product technologies is the Haldor Topsøe A/S developed SNOXTM technology, where a DeNO_x catalyst is combined with an SO₂ oxidation catalyst in series. By adding a wet sulphuric acid absorber (WSA), the produced sulphuric acid can be obtained in commercial quality. In this respect a realistic model for the used SO₂ oxidation catalyst is the molten salt-gas system MHSO₄-M₂S₂O₇-V₂O₅/SO₂-O₂-SO₃-H₂O-N₂ (M = alkali). Results of our multidisciplinary research on this system will be highlighted¹.

An example of further attempt to improve this technology is the molten vanadium pyrosulfate-based SO₂ electrochemical removal cell, originally invented by Winnick and coworkers². If this is successfully implemented into a SNOXTM-like system, the expensive and bulky WSA unit can be avoided. The cell works by first oxidizing the incoming SO₂ and O₂, using the molten electrolyte as a catalyst:

Simultaneously, an applied electric field will reduce O₂ on the cathode side:

So at the electrolyte/cathode interface a fast Lux-Flood acid base reaction will occur:

Due to the applied field, sulfate will migrate across the membrane and decompose on the anode side, in an almost opposite reaction:

Due to the rather complicated electrolyte mixture with V₂O₅ dissolved in several pyrosulfates and sulfates, a number of side reactions can occur. Previously³ these side

reactions could lead to increased impedance across the membrane, yielding excess over-potentials. Now, these side reactions have been avoided with a new complicated mixed molten salt electrolyte. Improved performance of the cell is shown in Fig. 1. However, still sufficient low emissions of SO_x have not been achieved.

Figure 1: SO₂ (a) and SO_x (b) outlets from cathode chamber from vanadium pyrosulfate-based SO₂ electrochemical removal cell, at different temperatures as a function of applied current density.

It is believed that this requires a new optimization of the ceramic structures of the inert membrane matrix holding the electrolyte, as well as the porosity of the electrodes, especially in the electrolyte-electrode interfaces. However, this process remains an interesting alternative method for efficient SO₂ removal – potentially a cheap way of achieving the desired waste-to-product technology.

Pressure swing adsorption (PSA) or temperature swing adsorption (TSA) processes, which are energy efficient and without by-product formation, can provide an excellent SO₂ resource for sulfuric acid production in an alternative waste-to-product approach⁴. Generally, however, it is difficult to find an adsorbent allowing reversible and selective adsorption of SO₂. For example, liquid amines trap acidic gasses such as, e.g. CO₂ and SO₂, too strongly by formation of stable ammonium carbonate and sulphite. Furthermore, in the case of large-scale SO₂ capture from flue gas, the relative volatile amines can evaporate into the gas stream.

Recently, Han and coworkers⁵ suggested an ionic liquid to chemically adsorb SO₂ to form a reversible compound. Hence, yet another promising flue gas cleaning technology can utilize the reversible absorption properties of certain ionic liquids. These can be used to selectively absorb either flue gas components NO or SO₂ into room (or low) temperature ionic liquids in a simulated power plant setup.

We will present new results on some ionic liquids performing as selective, reversible absorbers in PSA and TSA processes.

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