

Title: A process for catalytic filtration of sulfur-containing gases using selective catalytic reduction

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The present invention relates to a novel process for catalytic filtration of sulfur-containing gases using selective catalytic reduction (SCR) with catalyst regeneration using ozone injection.

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It is well known that when traditional SCR catalysts are in operation in sulfur-containing flue gases at low temperatures, formation of ammonium bisulfate (NH_4HSO_4) is an important issue regarding design and operation.

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Selective catalytic reduction is primarily a means of converting NO_x (nitrogen oxides) into N_2 and H_2O . A gaseous reductant, typically anhydrous ammonia, aqueous ammonia or urea, is added to a stream of flue gas or exhaust gas and then adsorbed onto a catalyst. When urea is used as the reductant, CO_2 is a reaction product.

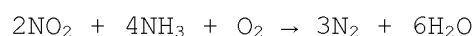
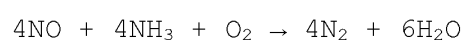
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SCR catalysts are made from various ceramic materials used as a carrier, such as titanium oxide, and active catalytic components are usually either oxides of base metals (such as vanadium, possibly augmented with molybdenum and/or tungsten), zeolites, or various precious metals (such as palladium and platinum). Another catalyst based on activated carbon, which is applicable for the removal of NO_x at low temperatures, has also been developed.

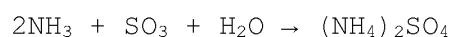
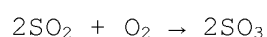
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The NO_x reduction reaction takes place as the gases pass through the catalyst chamber. Before entering the catalyst

chamber the ammonia, or other reductant (such as urea), is injected and mixed with the gases. The chemical equation for a stoichiometric reaction using either anhydrous or aqueous ammonia for a selective catalytic reduction process is as shown below:



with several secondary reactions:



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During the combustion process in a power plant, sulfur is concurrently formed with CO and hydrocarbons as various sulfur oxides (SO_x), typically around 97% SO₂ and up to 3% SO₃. Thus, fuel with a higher sulfur content tends to produce higher amounts of SO₃.

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As shown above, SO₃ can react with ammonia to produce ammonium sulfate ((NH₄)₂SO₄) and ammonium bisulfate (NH₄HSO₄). Certain SCR catalysts, such as vanadium-based catalysts, are particularly sensitive to contamination from ammonium sulfate and especially ammonium bisulfate, which is condensed in the pore structure of the catalyst at lower temperatures, thereby physically blocking the pores and deactivating the catalyst. On the other hand, operation of the

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SCR at a low temperature is desirable because it can provide higher efficiency for power production in the plant.

One proven way to handle this dilemma is to periodically
5 operate the SCR at a higher temperature, where the ammonium bisulfate is released from the catalyst and the catalyst pores are made available for the catalytic reaction. In this way, the catalyst is reactivated.

10 Catalytic bag filters in SCR service are often operating at low temperatures. For sulfur-containing gases, formation of ammonium bisulfate becomes a major cause for concern, often preventing any use of bag filter SCR. Generally, filter bags are stable up to around 230°C which makes periodic
15 heat treatment impossible.

The issue concerning formation of ammonium bisulfate when SCR catalysts are operated in sulfur-containing flue gases at low temperatures is known from the prior art. Thus, WO
20 2016/028290 describes an exhaust after-treatment system in which a sulfur trioxide trap, configured to selectively capture SO₃ from the exhaust gas, is included. This way, the formation of ammonium bisulfate is counteracted.

25 KR 2016 0102691 describes an apparatus and a method for regenerating an SCR system catalyst, which is done by controlled raising of the system temperature up to or above the temperature, at which ammonium bisulfate stuck in the catalyst pores becomes removable.

30 Further, various Chinese documents address the ammonium bisulfate removal issue. Thus, CN 1039 53420 (A) describes a

method and a device for the clearing of SCR catalyst sediment particles in the exhaust aftertreatment of a diesel engine, and CN 1039 20540 (A) describes a method and a device for regenerating an SCR denitration catalyst applied
5 to aftertreatment of diesel engine exhaust.

The idea underlying the present invention is to operate a catalytic bag filter in SCR below the dew point of ammonium bisulfate and periodically regenerate the catalyst using
10 ozone injection, thereby removing ammonium bisulfate from the catalyst pore structure.

From CN 1021 33547 (A) it is known to use an ozone treatment to regenerate a vanadium-titanium based flue gas denitration catalyst. The treatment method comprises filling an
15 inactivated flue gas denitration catalyst into a catalyst regeneration reaction bed, introducing a mixed gas of ozone and air into the reaction bed and finishing the catalyst regeneration after oxidation.

20 It is known in the art that ozone is a strong oxidant that can also increase the reactivity of catalysts to convert heavy hydrocarbons at room temperature. Ozone (trioxygen, O_3) is known as a strong oxidizing agent for waste and
25 drinking water treatment, sterilization and deodoration. It is an allotrope of oxygen that is much less stable than the diatomic allotrope O_2 , breaking down in the lower atmosphere to normal dioxygen. Since ozone is a powerful oxidant (far more so than dioxygen), it has many industrial applications related to oxidation. However, due to the fact that
30 ozone itself is toxic, the residual ozone from these oxida-

tion processes must be removed. Moreover, being quite harmful to animal and plant tissue even in concentrations as low as around 100 ppb, ozone is a pollutant that cannot be emitted. For these reasons, much research is devoted to
5 find suitable catalysts for oxidation reactions using ozone and also to find effective ways of removing residual ozone following such oxidation reactions.

In the presence of ammonia, the acid gases in the sulfur-
10 containing flue gas form ammonia salts, i.e. ammonium chloride (NH_4Cl), ammonium nitrate ($(\text{NH}_4)_2\text{NO}_3$) and ammonium bisulfate (NH_4HSO_4). In most cases, NH_4HSO_4 has the highest dew point, but in waste incineration units with HCl concentrations of several hundred ppm NH_4Cl , condensation deter-
15 mines the minimum temperature. SCR installations in coal fired power plants are normally operated at temperatures between 330 and 430°C with typical ammonium bisulfate catalyst dew points between 280 and 320°C. Below the dew point, ammonia and sulfuric acid condense as liquid ammonium bi-
20 sulfate in the catalyst pore structure, which will inhibit the catalyst performance. At sufficiently high temperatures, gaseous sulfuric acid is in equilibrium with SO_3 , and the ammonium bisulfate dew point therefore depends on water content, ammonia content and SO_3 concentration.

25 Ammonium bisulfate has a melting point of 147°C. Formation of ammonia sulfate ($(\text{NH}_4)_2\text{SO}_4$) is thermodynamically more favorable, but analysis of condensed salts has shown that the sulfate is only formed in limited amounts due to kinetic
30 limitations.

The inhibition of ammonium bisulfate is reversible, and the ammonium bisulfate is readily evaporated by increasing the catalyst temperature. The bulk dew point at the SCR reactor inlet is typically around 290°C, but the observed dew point
5 is higher due to capillary forces in the micropore structure. The ammonium bisulfate dew point decreases through the SCR reactor since ammonia is consumed in the SCR reaction.

10 The catalyst activity is directly related to the extent of pore condensation, which means that the ammonium bisulfate increases gradually as the temperature drops towards the bulk dew point. Operation below the bulk dew point is not an option, except for very low SO₃ concentrations in a low
15 dust SCR installation. This is because ammonium bisulfate will condense, not only inside the catalyst pores but also at the catalyst surface, thereby creating a sticky surface which - over time - could lead to plugging of the catalyst.

20 So the present invention relates to a process for catalytic filtration of sulfur-containing gases using a selective catalytic reduction (SCR) bag filter consisting of a substrate, a carrier and one or more catalytic materials, wherein

25 - the SCR bag filter is operated at a temperature below the dew point of ammonium bisulfate, and

- the catalyst is periodically regenerated using ozone injection,
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thereby removing ammonium bisulfate from the pore structure of the catalyst.

5 A selective catalytic reduction (SCR) bag filter to be used in the process of the invention preferably is in the shape of a filter bag assembly comprising multiple fabric filter bags coaxially arranged within an outer filter bag. Inside the outer filter bag, one or more inner tubular filter bags are separately installed within the outer filter bag and
10 within each other for the removal of dust and particulate matter in the process gas. At least one of the inner tubular filter bags and/or the outer tubular is/are provided with a catalytically active substance. The substrate of the catalyst substance is a fiber structure which can be e.g.
15 woven or knitted glass fibers, and the carrier can be titanium dioxide or another suitable compound. Typically, the SCR catalyst will consist of a carrier (TiO_2) and a catalytic material comprising vanadium pentoxide (V_2O_5). The catalytic material can also comprise other compounds, such
20 as W and/or Mo oxides.

Bag filters are well suited for the removal of dust and particulate matter from gas streams. Catalytic bag filters
25 have the double utility of being able both to remove particulates from a gas stream and to catalyze one or more desired reactions in the gas. A catalytic bag filter can comprise one single layer of filter fabric, but it will typically comprise two or three layers of filter fabric, each
30 layer containing a tailored catalyst optimized for removal of a specific kind of compound from the gas that passes through it. Dust and other particulate matter will settle

on the surface of the outer bag, from where it can easily be removed. The two or three-layer structure provides the flexibility to tailor different catalytic combinations for different purposes. One of the layers of the catalytic filter bag serves the primary purpose of reducing residual ozone.

The term "outer bag" refers to the filter bag through which the process gas passes first, and the term "inner bag" refers to the filter bag(s) through which the process gas passes subsequently after having passed through the outer bag.

The catalytically active material in at least one of the one and more tubular inner filter bags and/or the outer tubular filter bag is a catalyst composition comprising a vanadium oxide and titania.

The term "a vanadium oxide" refers to:
vanadium(II)oxide (vanadium monoxide), VO ;
vanadium(III)oxide (vanadium sesquioxide or trioxide), V_2O_3 ;
vanadium(IV)oxide (vanadium dioxide), VO_2 ; or
vanadium(V)oxide (vanadium pentoxide), V_2O_5 .

The preferred vanadium oxide for use in the process of the invention is vanadium pentoxide (V_2O_5).

The term "titania" refers to titanium dioxide (TiO_2).

The catalytically active material can further comprise palladium or platinum in metallic and/or oxidic form.

These catalysts are active both in the removal of VOCs and carbon monoxide and in the removal of nitrogen oxides (NO_x) by the SCR reaction with NH₃.

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The Pd/V/Ti catalyst is a preferred catalyst because (i) it has a dual functionality (removal of NO_x and removal of VOCs), (ii) it is sulfur-tolerant, and (iii) it has a lower SO₂ oxidation activity compared to other catalyst compositions.

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It is known that the oxidation activity of a Pd-containing catalyst is reduced in the presence of a few ppm of NH₃. It is also known that, besides being an active catalyst in the NH₃-SCR of NO_x, vanadium oxide is also an active oxidation catalyst. Compared to the precious metal catalysts, like the Pd catalyst, the vanadium oxide catalyst is less selective in the formation of CO₂, and some CO is produced during the oxidation reactions. CO cannot be oxidized to CO₂ at a feasible reaction rate by contact with the vanadium oxide catalyst, but requires presence of a noble metal catalyst, such as Pd. Thus, if NH₃ is present in the gas, then it is preferred to catalyze the outer filter bag with a V/Ti catalyst and at least one of the inner filter bags with a Pd/V/Ti catalyst if CO is present in the process gas or formed by the catalytical oxidation of VOCs in the outer filter bag. Thus, by loading an inner filter bag with a Pd/V/Ti catalyst, CO and any remaining VOCs will effectively be oxidized to CO₂. In this way, the load of expensive noble metals in the inner filter bags can be limited to a minimum.

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The outer tubular filter bag and the one or more inner tubular filter bags can be installed in a tube sheet to form a tubular filter bag assembly, wherein a first inner tubular bag, having a smaller diameter than the outer bag, is separately arranged inside the outer bag which forms an effective seal between the dirty side and the clean side of the filter.

The next inner tubular bag, with a diameter less than those of the outer bag and the first inner bag, is then separately arranged within the previous inner bag. Optionally more than two inner bags may be arranged in the filter bag assembly.

Any dust and particles present in the process gas will be deposited on the outer surface of the outer tubular filter bag facing the gas. Thus, the catalysts loaded onto the outer bag and/or the inner bag(s) are effectively protected against potential catalyst poisons present in the particles contained in the process gas.

In the process of the invention, the catalyst is periodically regenerated with ozone, whereby ammonium bisulfate is removed from the pore structure of the catalyst.

When the catalyst is regenerated with ozone, the regeneration is conducted in reverse flow through the catalytic filter bag, i.e. from the center of the bag through the bag and into the bag house or chamber.

The ozone to be injected can come from various sources, such as an ozone generator. Ozone generators are available

in full industrial size, and they are widely used, such as in the pulp and paper industry.

The operation temperature of the process of the invention
5 is above the solidification temperature of ammonium bisulfate, i.e. above 147°C.

Claims:

1. A process for catalytic filtration of sulfur-containing gases using a selective catalytic reduction (SCR) bag filter consisting of a substrate, a carrier and one or more catalytic materials, wherein
 - the SCR bag filter is operated at a temperature below the dew point of ammonium bisulfate, and
 - the catalyst is periodically regenerated using ozone injection,thereby removing ammonium bisulfate from the pore structure of the catalyst.
2. Process according to claim 1, wherein the SCR bag filter is an assembly consisting of an outer tubular filter bag and one or more inner tubular filter bags installed in a tube sheet.
3. Process according to claim 1 or 2, wherein the catalyst consists of a carrier and one or more catalytic materials.
4. Process according to any of the claims 1-3, wherein the carrier is TiO_2 , and the catalytic materials are selected from the vanadium oxides VO , V_2O_3 , VO_2 and V_2O_5 .

5. Process according to claim 3 or 4, wherein the catalyst further comprises Pd in metallic or oxidic form.
- 5 6. Process according to claim 1, wherein one layer of the SCR bag filter serves the primary purpose of reducing any residual ozone.
- 10 7. Process according to claim 1, wherein the operation temperature is above the solidification temperature of ammonium bisulfate.
- 15 8. Process according to claim 1, wherein the catalyst is periodically regenerated with ozone, thereby removing ammonium bisulfate from the pore structure of the catalyst.
- 20 9. Process according to claim 8, wherein the ozone regeneration is conducted by flowing ozone through the SCR bag filter from the clean side thereof.