FAST-REGENERABLE SULFUR DIOXIDE ADSORBENTS FOR DIESEL ENGINE EMISSION CONTROL

This invention was made with Government support under Contract DE-AC06-76RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD

This disclosure relates to emissions control, particularly the control of sulfur oxide emissions using regenerable sulfur dioxide sorbents.

BACKGROUND

The emission of pollutants such as sulfur oxides and nitrogen oxides in combustion waste gases causes serious environmental problems. Major efforts are underway to reduce these emissions through the implementation of particulate filters and NO_x conversion devices. One promising approach to minimizing NO_x emissions involves capturing and storing NO_x as an alkali or alkaline earth nitrate during normal operation (lean conditions) and releasing the stored NO_x after reducing it to molecular nitrogen (N_2) under fuel-rich conditions.

Sulfur oxides (SO_x) are produced as combustion byproducts and interfere with the function of current NO_x traps by reacting with NO_x catalytic components, degrading or "poisoning" the trap. Sulfur dioxide also reacts with the oxidants present in particulate filters, yielding sulfur trioxide, sulfuric acid particulates and depositing sulfate salts on the catalyst, which degrades the effectiveness of the particulate filter. Despite the recent introduction of low sulfur diesel fuels, the 15 ppmw (parts per million by weight) concentration of sulfur in these fuels still overwhelms current NO_x traps and particulate filters.

Current sulfur absorbent technology has significant limitations. For example, copper-doped alumina ($Cu—Al_2O_3$) has been studied as a regenerable flue gas sulfur oxide absorbent. It reacts with SO_2 and O_2 at ~350° C. to form $CuSO_4$ and $Al_2(SO_4)_3$. The sulfated absorbent can be regenerated by reduction in H_2 or CH_4 at 400-500° C., followed by oxidation in air at 500° C. to reform the copper oxide phase. The chemistry involved in the absorption/regeneration cycle makes it extremely challenging to use Cu-doped Al_2O_3 as an on-line regenerable sulfur trap for diesel emission aftertreatment systems, due to the copper oxide/copper metal redox that is taking place in parallel with the sulfate adsorption and desorption. The unsulfated CuO will react with rich gas to form metallic Cu, which not only causes a fuel penalty, but also prevents the system from fast regeneration because copper oxide reduction competes kinetically with copper sulfate reduction. Thus, high loadings of copper do not provide an advantage in the preparation of the absorbent.

SUMMARY

Disclosed herein are sorbents and devices for controlling sulfur oxides emissions as well as systems including various embodiments and combinations of such sorbents and devices. Also disclosed are methods for using the disclosed sorbents, devices and systems in emissions control that overcome many of the limitations of current technologies for sulfur dioxide control. Also disclosed are methods for making and using the disclosed sorbents, devices and systems.

In one embodiment, emission control devices disclosed herein include sorbent beds or traps for absorbing sulfur dioxide. In one embodiment such devices include a sorbent material comprising first and second catalytic materials and a carrier. The first catalytic material is a precious metal, which typically is present in from about 0.1 weight percent to about 10 weight percent. Examples of suitable precious metals include, without limitation those such as platinum, palladium, ruthenium, rhodium and combinations thereof. The second catalytic material is silver, typically present in from about 1 weight percent to about 50 weight percent.

In further embodiments, a disclosed emission control device is included in a system for emissions control. In one example, such systems include first and second emission control devices fluidly connectable to a combustion exhaust stream source wherein the first emission control device comprises a sorbent material comprising from about 0.1 weight percent to about 10 weight percent platinum and from about 1 to about 50 weight percent silver and a carrier. Such systems may have the first emission control device arranged upstream of the second emission control device. In one embodiment the upstream, first emission control device comprises a sulfur dioxide trap.

One embodiment of the disclosed systems includes one or more regenerable sulfur dioxide traps, such as regenerable sulfur dioxide traps, including those that can be regenerated during a normal cycle of the combustion exhaust stream.

The carrier component of the disclosed sulfur dioxide sorbents may optionally be formed into or on a porous substrate. In such examples, the precious metal and/or silver constituents may be impregnated into or deposited on the carrier before or after deposition onto the porous substrate. Likewise, the precious metal and/or silver constituents may be mixed with the carrier, including intimately mixed with the carrier before the carrier is formed into a porous substrate.

Methods for using the disclosed sorbents may include a method for emissions control wherein a combustion exhaust stream is contacted with a sulfur dioxide sorbent including a precious metal and silver at a location upstream of a NO_x trap. In one embodiment, this method results in more efficient operation of the NO_x trap due to the removal of interfering sulfur compounds. In another aspect of a disclosed method the sorbent is regenerated by contacting it with a rich combustion waste stream, such as a combustion waste stream comprising less than about 1 molar percent oxygen.

Also disclosed herein are low emission motor vehicles, wherein the combustion engine that powers the vehicle is coupled to an emission control device containing a sorbent comprising both silver and a precious metal. This emission control device is further coupled to a downstream emission control device for removing NO_x and/or particulates. The presently disclosed sorbents, emission control devices and systems can be used to reduce emissions from any waste stream source. In one aspect, the disclosed materials, devices and systems are particularly well-adapted for use with diesel combustion engines.

The foregoing and other objects, features, and advantages of the invention will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.