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Hydrotalcite sulfur oxide sorption

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<b>(21) International Application Number:</b> PCT/US97/09809 <b>(22) International Filing Date:</b> 19 June 1997 (19.06.97) <b>(30) Priority Data:</b> 60/020,126 20 June 1996 (20.06.96) US <b>(71) Applicant:</b> CONTRACT MATERIALS PROCESSING, INC. [US/US]; 1922 Benhill Avenue, Baltimore, MD 21226 (US). <b>(72) Inventors:</b> ALBERS, Edwin, W.; 1922 Benhill Avenue, Baltimore, MD 21226 (US). BURKHEAD, Harry, W., Jr.; 1922 Benhill Avenue, Baltimore, MD 21226 (US). <b>(74) Agent:</b> WISE, L., Gene; Suite 101, 1364 Beverly Road, McLean, VA 22101-3628 (US).	<b>(81) Designated States:</b> AU, CA, JP, MX, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> HYDROTALCITE SULFUR OXIDE SORPTION <b>(57) Abstract</b> <p>Hydrotalcite-like materials are stable in the crystalline oxide structure and essentially reversible in anion exchange. A novel process of sulfur oxide sorption is provided utilizing these hydrotalcite materials as contact solids. Large crystalline sheet materials having increased sorption of SO<sub>x</sub> are provided by incorporation of certain organic acid anionic species to modify the hydrotalcite/brucite structure. Typical industrial applications include sulfur removal from fluid catalyst cracking process, cold-side combustion gas sulfur abatement and cleaner coal gasification.</p>		

HYDROTALCITE SULFUR OXIDE SORPTIONFIELD OF THE INVENTION

5 The present invention relates to new hydrotalcite sorbents useful in sulfur abatement and novel processes.

BACKGROUND OF THE INVENTION

10 Industry is lacking a composition such as fluidized bed catalyst or additive contact solids for economically removing sulfur oxides from emissions from a variety of industrial processes. Further, the industry lacks effective and economical methods for using a fluidized bed of particles to remove sulfur oxides from emissions.

15 Synthetic hydrotalcites, known as layered double hydroxides, are useful as contact solids in numerous industrial processes. In view of a limited supply of naturally-occurring hydrotalcite, various efforts have been made to achieve a reasonably economic alternative material in the form of synthetic Layered Double Hydroxides ['LDH'].

20 Production of analogous crystalline materials has been fruitful, and it may be expected that important new uses for the class of hydrotalcite crystalline solids will increase industrial demand.

25 The 'hydrotalcite-like' materials of Shutz et al are characterized by crystals having very high broadness to thickness ratios in the 50:1 to 5000:1 range. These interesting materials have desirable mechanical and chemical properties, which will render them useful as a solids binders or as active chemical sites. Recent efforts  
30 in this aspect of layer propagation have identified certain

5 anionic species which contribute to forming the large  
sheets of synthetic hydrotalcites. The mechanism whereby  
these lower alkanolic acid anions direct the important plate  
shape is not understood; however, large plate crystals  
having a maximum dimension of about 5 to 500 microns ( $\mu$ )  
10 impart excellent mechanical properties.

A structural description of the class of "brucite"  
crystals is found in the work of Pinnavaia et al (U.S.  
Patent No 5,358,701, incorporated by reference). Briefly,  
the metal oxide layers consist essentially of magnesium  
15 oxide (MgO) configured structurally with octahedral hydroxy  
groups. A trivalent metal oxide, such as alumina ( $Al_2O_3$ ),  
can be inserted into the brucite crystalline lattice in the  
octahedrally-coordinated metal oxide layer. In the case of  
natural hydrotalcite, the carbonate layer or gallery may be  
20 replaced by substitution of various acidic anions, sulfate,  
sulfite, nitric, etc.

#### SUMMARY OF THE INVENTION

It has been discovered that incorporation of certain  
25 organic acid anionic species can be effective in modifying  
the hydrotalcite/brucite structure to result in large  
crystalline sheet materials having increased sorption of  
 $SO_x$ . Since hydrotalcite-like materials are stable in the  
crystalline oxide structure and essentially reversible in  
30 anion exchange up to about 400°C, stable sorbent may be  
employed in moderately elevated industrial processes, such  
as cold side combustion effluent treatment of fossil fuel  
burning power plants.

5           In a preferred embodiment of the invention, a novel  
process of sulfur oxide sorption is provided, wherein a  
gas containing sulfur oxide is contacted at process  
temperature, from about 200°C up to about 950°C with a solid  
10           sorbent material to remove sulfur oxide from the gas. The  
improvement comprises utilizing a solid sorbent material  
comprising at least one layered hydrotalcite sheet having a  
brucite crystalline structure containing divalent and  
trivalent metal oxides comprising predominantly magnesia  
and alumina present in the brucite structure in molar ratio  
15           of 3:1 to 8:1 magnesia:alumina, together with a sulfur  
oxide replaceable anion, the hydrotalcite sheet having a  
breadth to thickness ration of 50:1 to 5000:1. The amount  
of hydrotalcite in the solid sorbent can vary from about 10  
to 100 wt%.

20           Sulfur oxide sorption may be enhanced by depositing on  
the hydrotalcite-containing solid sorbent material an  
effective amount (eg- 50 to 500 ppm) of oxidative metal  
catalyst, such as platinum. In one embodiment the solid  
sorbent material comprises at least 10 wt% hydrotalcite and  
25           10 to 50 wt% of a ZnO:TiO<sub>2</sub> sorbent mixture.

The invention also includes a process for reducing the  
amount of SO<sub>x</sub> emissions passing through a fluidized  
particle bed.

30           DETAILED DESCRIPTION OF THE INVENTION

In the following description, units are given as parts  
by weight and metric units unless otherwise indicated.

5     Process Applications: - The present invention relates to fluidizable catalysts or contact solids, methods for using such materials to reduce the emissions of sulfur compounds from industrial processes, and methods for preparing such contact solids or catalysts with hydrotalcite.

10           The conversion, processing or burning of sulfur-containing fossil fuels can result in the emission of sulfur-containing compounds, such as H<sub>2</sub>S and SO<sub>x</sub>, to the atmosphere. To comply with increasingly stringent environmental regulations, materials are sought to  
15     reduce the emissions of sulfur compounds from industrial processes. Several methods of desulfurization are currently being used commercially. These methods include flue gas scrubbing as well as various fixed bed, ebullating bed, and fluid bed catalytic reaction processes. Some of  
20     these processes treat the flue gas just prior to the release of gas to the atmosphere.

          Other processes are performed upstream of the emission release in order to prevent the undesired emission from occurring. The goal of such processes is to reduce  
25     emission of sulfur-containing compounds into the atmosphere.

          The inventive process reduces the amount of SO<sub>x</sub> emissions passing through a fluidized particle bed. This process may comprise the step of introducing into the fluid  
30     particle bed a microspheroidal catalyst having a composition comprising at least 10 wt% of SO<sub>x</sub>-capturing hydrotalcite-type metal oxide. Typically, this involves sorbing or capturing SO<sub>2</sub> in the fluid particle bed regenerator as an inorganic sulfate in a fluid cracking

5 catalytic operation. In a petroleum refinery SOx emissions are often generated in the fluid cracking catalyst regenerator and released in its flue gas.

A typical sulfur abatement process includes the step of introducing into the fluid particle bed a  
10 microspheroidal catalyst having a composition comprising at least one SOx-capturing oxide and at least one inorganic binder. Oxidation of SO<sub>2</sub> to SO<sub>3</sub> can be achieved employing an oxidation promoter catalytic component in a fluid particle bed, such as FCC regenerator.

15 The sulfur-laden hydrotalcite crystalline sheet material is a novel composition containing a sulfate anionic crystal moiety having at least 5 weight percent sulfur oxide based on sulfur-free hydrotalcite. The capture of SO<sub>3</sub> in the fluid particle bed regenerator as an  
20 inorganic sulfate on the SOx-capturing oxide is usually followed by reducing the inorganic sulfate to a sulfide in a fluid particle bed reactor/stripper. Then, the sulfur can be released as H<sub>2</sub>S upon hydrogenolysis or reduction in the stripper. Incorporation of a minor amount of a  
25 vanadium oxide component in the contact solids promotes reduction of sulfate during regeneration of the hydrotalcite.

The catalyst composition is desirably formed into a fluidizable particle having an average particle size in the  
30 range of about 20-300μ that is useful in both conventional fluidized bed and ebullating bed processes. The SOx-capturing oxide of the invention is desirably a sheet-like hydrotalcite and/or mixed inorganic oxide additive for catalyzing the capture and release of sulfur-containing

5 compounds in the fluid cracking catalyst provides refiners  
with an effective means for reducing fluid cracking  
catalyst SOx emissions. The invention provides a contact  
solids or catalyst composition employed as a formed  
spheroidal catalyst that reduces the emissions of sulfur  
10 containing compounds from industrial processes.

For example, in the preferred embodiment of the  
invention, the hydrotalcite captures and thereby removes  
the sulfur containing species, such as H<sub>2</sub>S or SOx that is  
present in the gas stream being treated.

15 The hydrotalcite composition may include a combination  
of inorganic oxides with an inorganic binder, an organic  
binder, or a mixtures of an inorganic and organic binder.  
Desirable inorganic oxides include a member selected from  
the group consisting of oxides or hydroxides of aluminum,  
20 calcium, cobalt, copper, iron, magnesium, molybdenum,  
silicon, titanium, vanadium, zinc, tungsten, strontium,  
nickel, manganese, zirconium, barium, members of the  
lanthanide series and mixtures thereof.

The contact solid composition may be self-bound or may  
25 include a binder component to "glue" the inorganic oxides  
together into the desired shape, such as spheroidal  
particles. Depending on the application, different binding  
systems are used. For example, in more severe high  
temperature applications such as fluid cracking catalyst  
30 (eg- 700-820°C), a hydrothermally stable inorganic binder  
such as aluminum chlorohydrol or peptized alumina is used.

Effective inorganic binders include sols of aluminum  
such as aluminum chlorohydrol, peptized aluminas, sols of  
silica, colloidal silicas, sols of titanium, sols of



5 zirconium clays such as bentonite, calcined kaolinite,  
kaolinite, metakaolin, montmorillonite, chlorite, talc, and  
mixtures of these. Desirable inorganic binders include a  
sol of aluminum, peptized alumina, a sol of silica,  
colloidal silica, a sol of titanium, a sol of zirconium, a  
10 clay, and mixtures thereof.

The smectite clays are especially desirable alone or  
in combination with zinc oxide/titania mixtures, various  
inorganic binders and smectite. In some applications, such  
as a fluidized or ebullating bed, found in many flue gas  
15 desulfurization units, an organic binder such as  
hydroxypropyl methyl cellulose or polyvinyl alcohol is  
used.

Other components can be added to the catalyst  
composition to enhance the performance of conversion  
20 catalyst in specific applications or for a specific set of  
operating conditions. An oxidation promoter such  
as platinum or cerium can be added to the catalyst solids  
to facilitate the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , for instance in  
the fluid cracking catalyst regenerator, thus improving the  
25 overall performance of the catalyst. Desirable additional  
components can include any number of activators, promoters  
oxidizers, reducers, scavengers, and mixtures of these  
components. These materials may enhance performance. The  
solid composition preferably is prepared in the form of a  
30 spheroidal particle of about 1 to 10,000 microns diameter.

Advantageously, this invention is employed to reduce  
emissions of sulfur compounds from a fluid cracking  
catalyst (FCC) process. Particulate solids are added to  
the FCC unit in the same manner as the conventional

5 cracking catalyst (eg- REY zeolite). The hydrotalcite  
additive can be introduced separately or together in a  
mixture with the cracking catalyst. Usually the addition  
is accomplished by a pneumatic conveying system to blow the  
material directly into the FCC catalyst regenerator. The  
10 catalyst additive then circulates through the fluid  
cracking catalyst unit in direct contact and along with the  
fluid cracking catalyst. The quantity of fluid cracking  
catalyst additive that is added and which then circulates  
in the unit is sufficient to effectively reduce the  
15 emissions of sulfur containing compounds from the FCC unit,  
yet it need not be present in a proportion so large that it  
deleteriously affects the operation of the cracking process  
reactions. Fluid cracking catalyst additive level of  
between about 0.5 and about 10 weight percent of the  
20 circulating fluid cracking catalyst inventory is desirable.

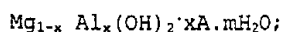
In the coal gasification process, the flue gas or hot  
gas is passed through a fluidized or ebullating bed of  
catalyst to remove sulfur compounds.

Industrial processes for sulfur oxide abatement may be  
25 conducted at various temperatures. Whereas cold side flue  
gas abatement may be carried out advantageously at about  
200 to 400°C, more elevated temperatures in the 400 to 700°C  
range may be employed. FCC processes may employ the  
hydrotalcite sorbents at 700 to 820°C or higher  
30 temperature, as will be understood by the skilled chemical  
engineer.

Synthesis Methods: A preferred method of manufacturing

5 hydrotalcite-like materials having a sheet morphology is disclosed by Shutz et al in U.S. Patents No. 5,399,329 and 5,507,980, incorporated herein by reference. These materials may be synthesized from an aqueous slurry of pseudoboehmite and magnesia in the presence of C1-C6 lower  
10 monocarboxylic acid, such as acetic acid. The coprecipitated crystalline sheet materials have a very high breadth:thickness ratio, eg- 50:1 to 5000:1.

The process of sulfur oxide sorption is preferably carried out by a hydrotalcite having the following formula,  
15 as synthesized:



where A is a lower monocarboxylic anion,  
x is 0.2 to 0.4, and m is 0 to 4.

Divalent Mg may be substituted in the brucite  
20 crystalline structure up to 50 mol% by other divalent metal cation, such as Ni, Cu, Zn, Co and/or Mn; and Al ion may be substituted in the brucite crystalline structure up to 50 mol% by trivalent metal cation, such as Cr and/or Fe.

Sulfur oxide sorption may be enhanced by depositing on  
25 the hydrotalcite-containing solid sorbent material an effective amount (eg- 50 to 500 ppm. Pt) of oxidative metal catalyst, such as platinum, palladium, cerium, etc. This is believed to permit sulfur dioxide to be oxidized to sulfur trioxide to provide a sulfate ion in the sorbent  
30 lattice as a 'gallery layer' anion.

#### Sulfur Oxide Sorption -

It is understood that hydrotalcite crystalline material may have up to four moles of water bound to the

5 ideal formula unit moiety of the crystals. Accordingly,  
there is a significant weight decrease when water of  
hydration is lost during heating to about 200-400°C.

It is known that natural hydrotalcite and other LDH  
materials are sorbents for sulfur dioxide (SO<sub>2</sub>) and sulfur  
10 trioxide (SO<sub>3</sub>), collectively - "SO<sub>x</sub>". According to  
Pinnavaia et al (US Patent 5,358,701), these sulfur oxides  
can replace the carbonate anion moiety or other anions in  
the brucite lattice in the temperature range of 100°C to  
400°C. A standard test method for measuring such sorption  
15 characteristics is thermogravimetric analysis (TgA),  
wherein a test sample of the crystalline solid material is  
heated at predetermined rate to 700°C, releasing water of  
hydration. A gaseous stream containing the sulfur oxide is  
then contacted with the sample and weight of sorbed  
20 material is measured. Regeneration of the sorbent (ie- by  
reduction of sulfate to sulfite) can be effected by passing  
a hot gas, such as hydrogen over the sample.

In the following examples, various contact solids test  
by TgA for comparing SO<sub>x</sub> sorption in a controlled heating,  
25 sorption and regeneration cycle. A standard duPont TgA  
unit is employed to test samples in the TgA ramp method.  
The sample is heated at uniform rate to 700°C with a  
flowing stream of nitrogen through the sample. The  
sorption cycle employs 3000 ppm. SO<sub>2</sub> in a carrier gas  
30 stream containing 3 wt% oxygen and balance nitrogen and  
maintains the sample at predetermined temperature of 700°C  
for at least 30 minutes during sulfur oxide sorption.

5       Regeneration is performed by hot hydrogen gas flowing over  
the sample at 650°C.

10       Example 1 - A mixed hydrotalcite-Pt contact solid is  
tested by standard TgA method. The sheet-type hydrotalcite  
component (invention) comprises LaRoche HTC powder having a  
particle size range of about 4 to 90 microns (predominantly  
15-40 microns), produced by the method of US Patent  
5,399,329. The hydrotalcite powder is blended with equal  
parts of spheroidal oxidation catalyst component containing  
15       550 ppm Pt on alumina substrate to provide a 50:50  
admixture having average 225 ppm. Pt, based on total  
sample. SO<sub>x</sub> sorption peaks at 17 weight percent (based on  
HTC) in 35 minutes and is released slowly during  
regeneration.

20       Example 2 - A comparative sample material is employed  
containing 'DESOX' spinel (MgAl<sub>2</sub>O<sub>4</sub>), a standard commercial  
desulfurization solid having 225 ppm. Pt deposited thereon.  
The procedure of Example 1 is repeated employing the  
25       standard sample.

30       Example 3 - An unmodified hydrotalcite powder sample  
as in Example 1 is tested for SO<sub>x</sub> sorption without Pt  
catalyst.

Example 4 - A zinc oxide/titanium dioxide mixture  
having a 1.5:1 ZnO:TiO<sub>2</sub> wt.ratio (35 wt%) is blended with  
10 wt% hydrotalcite powder as in Example 1, 15 wt% talc and  
40 wt% fine kaolin clay.

5

Table I

<u>Ex. No.</u>	<u>Description of Material(s)</u>	<u>Results</u>
1-	Hydrotalcite + Pt	17% pick-up
2-	Spinel + Pt (WR Grace DESOX)	17% pick-up
3-	Hydrotalcite (LaRoche HTC/ex. 1)	<1% pick-up
4-	ZnO:TiO <sub>2</sub> + HTC + talc + kaolin	9% pickup

Improved oxidation/sorption performance may be obtained by incorporating the Pt component directly onto the hydrotalcite-containing particles. Cerium and vanadium oxide are also suitable oxidation/reduction components.

In one aspect, this invention includes processes for producing the hydrotalcite solids. Typical methods include spray drying to make small (eg- 20-300 $\mu$ ) microspheroidal particles and beading or tumbling processes to make larger spheroidal particles.

While the invention has been shown by particular examples, there is no intent to limit the inventive concept, except as set forth in the following claims.

comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof



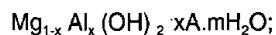
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process of sulfur oxide sorption wherein a gas containing sulfur oxide is contacted at elevated process temperature with a solid sorbent material to remove sulfur oxide from the gas, wherein:

solid sorbent material includes at least one layered hydrotalcite crystalline sheet having a brucite crystalline structure containing divalent and trivalent metal oxides including predominantly magnesia and alumina present in the brucite structure in molar ratio of 3:1 to 8:1 magnesia:alumina, together with a sulfur oxide replaceable anion, said hydrotalcite crystalline sheet having a breadth to thickness ratio of 50:1 to 5000:1.

2. The process of sulfur oxide sorption according to claim 1 wherein said solid sorbent material has deposited thereon an effective amount of oxidative metal catalyst.

3. The process of sulfur oxide sorption according to claim 1 wherein said hydrotalcite, as synthesized, has the formula:



where A is a lower monocarboxylic anion,

x is 0.2 to 0.4, and m is 0 to 4.

4. The process of sulfur oxide sorption according to claim 1 wherein Mg is substituted in the brucite crystalline structure up to 50 mol% of the Mg by divalent metal cation; wherein A is acetate ion; and wherein Al is substituted in the brucite crystalline structure up to 50 mol% by trivalent Cr or Fe metal cation.

5. A process of cracking a heavy hydrocarbon feed stock containing sulfur compounds, wherein a gas phase containing sulfur oxide is contacted at process temperature in the range of 700 to 820°C with a solid sorbent material to remove sulfur oxide from the gas, and wherein: said solid sorbent material includes at



least one layered hydrotalcite sheet having a brucite crystalline structure containing divalent and trivalent metal oxides including predominantly magnesia and alumina present in the brucite structure in molar ratio of 3:1 to 8:1 magnesia:alumina, together with a sulfur oxide replaceable anion, said hydrotalcite sheet having a breadth to thickness ratio of 50:1 to 5000:1.

6. A process for sulfur dioxide abatement including:

contacting a gaseous body containing sulfur dioxide at elevated process temperature with a solid sorbent material to remove sulfur dioxide from the gas;

said solid sorbent material including at least one layered hydrotalcite sheet having a brucite crystalline structure containing divalent and trivalent metal oxides including predominantly magnesia and alumina present in the brucite structure in molar ratio of 3:1 to 8:1 magnesia:alumina, together with a sulfur oxide replaceable anion, said hydrotalcite sheet having a breadth to thickness ratio of 50:1 to 5000:1.

7. The process of claim 6 for sulfur dioxide abatement wherein the gaseous body includes a vapor phase in the fluidized bed cracking of hydrocarbons; and wherein sulfur dioxide is formed and then converted at elevated process temperature of about 700 to 820°C, with a solid sorbent material having an oxidation metal to convert sulfur dioxide to sulfur trioxide, wherein the sulfur trioxide is captured by the hydrotalcite as gallery sulfate anion.

8. The process of claim 6 for sulfur dioxide abatement wherein the gaseous body is a coal combustion effluent stream; and wherein sulfur dioxide is converted to sulfur trioxide with an oxidation promoter at temperature of about 200 to 400°C.

9. The process of claim 7 wherein the solid sorbent material has deposited thereon an oxidation metal, and wherein sulfur trioxide is sorbed as sulfate anion.





10. The process of claim 8 wherein sulfur trioxide laden hydrotalcite is regenerated by reduction of sulfate to sulfide.

11. The process of claim 6 wherein the solid sorbent material includes at least 10 wt% hydrotalcite and 10 to 50 wt% of a ZnO and TiO<sub>2</sub> mixture.

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