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The Mobil Oil SO_x Treatment Process (MOST). Catalytic removal of SO_x and H_2S from refinery tailgas

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Abstract

Growing concerns about the environmental impact of sulfur emissions from stationary sources, as well as recent regulatory initiatives, have prompted investigations for advanced sulfur reduction strategies. Herein, we present a novel process/catalyst combination for reducing tailgas SO_x and H_2S emissions to very low levels (1–5 ppmw). The Mobil Oil SO_x Treatment Process (MOST) consists of the following steps: (1) combustion of tailgas sulfur species to convert all sulfur species to SO_2/SO_3; (2) adsorption of SO_x onto a high-capacity sorbent; and (3) in a separate step, reductive desorption of the sulfur as a concentrated stream of mainly SO_2 and H_2S. The MOST Process utilizes a regenerable promoted spinel-based sorbent with very high SO_x uptake capacities (>50 wt%), and is both, robust and operationally simple. Catalyst selection, process scoping studies, and characterization to help understand the nature of the oxidative sorption and reductive regeneration steps, as well as the state of the sorbent during these steps, are described. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen sulfide; SO_x removal; Spinel sorbent; Claus reaction; Emissions

1. Introduction

In conventional refining applications, sulfur is removed from hydrocarbon streams by reductive processes, such as catalytic hydroprocessing and catalytic cracking, to yield hydrogen sulfide. The hydrogen sulfide thus produced is typically collected by contact with an amine-based solution [1]. Subsequent stripping of the amine solution yields a concentrated acid gas stream, which is fed to a Claus plant. In the Claus plant, about a third of the hydrogen sulfide is combusted to form sulfur dioxide, which is then reacted with the remaining hydrogen sulfide to yield elemental sulfur and water. Because of equilibrium limitations, only ca. 97% of the feed sulfur is recovered in a Claus unit.

The remainder of the sulfur from such processing must be treated prior to release to the atmosphere. Two common types of tailgas treatment processes are the Beavon/Stretford and selective amine adsorption processes [2]. Both of these processes involve wet scrubbing, require hydrogen, and may be energy and labor intensive. Both of these processes can reduce sulfur emissions to several ppm, but are less effective in removing CS_2 or COS, or mitigating any CO which may pass through the Claus plant.

A solid sorbent system which can combust the sulfur containing species and selectively capture the SO_2 produced offers operational advantages over these wet scrubbing processes. Herein, we describe a novel process and catalyst combination, the Mobil Oil SO_x Treatment Process (MOST) for achieving these goals [3]. This process consists of the following steps:

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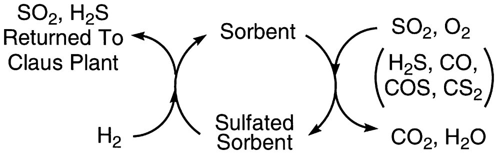

Scheme 1. The MOST Process for SO_x removal in claus tailgas operations.

(1) combust the Claus tailgas stream to raise its temperature, convert all sulfur species (H_2S and residual COS and CS_2) to SO_2/SO_3, and convert CO to CO_2;
(2) adsorb the SO_x onto a high-capacity solid sorbent, in either a fixed, moving, or fluidized bed; and
(3) in a separate step (for swinging fixed beds) or in a separate vessel (for moving or fluidized beds), reductively desorb the sulfur from the solid as a concentrated stream of mainly SO_2 and H_2S, which can then be recycled to the Claus unit for further processing.

In this contribution, we describe the MOST process. We discuss the oxidative sorption step, including catalyst selection and characterization. The reductive desorption of sulfur species is discussed by describing both the products and the thermodynamics of the regeneration. We also include a brief discussion of the MOST process configuration.

2. Results and discussion

The MOST process scheme for Claus tailgas treatment is illustrated in the catalytic cycle shown in Scheme 1.

Here, we describe the first step in this process scheme — the oxidative sorption of sulfur oxides under conditions suitable for Claus tailgas operation, sorbent screening for this application, and a brief description of the reaction chemistry.

2.1. Catalyst screening

Several potential sorbent candidates were chosen, based on a desire to obtain high SO_x uptakes per weight of catalyst employed. The base materials chosen for this application were high surface area alumina and magnesium aluminate spinels ($MgAl_2O_4$ and $Mg_2Al_2O_5$), with ceria, vanadia, and/or platinum as oxidation promoters. Conditions chosen for this screening applications are 1200°F and 3500 GHSV, with a feed containing 1% SO_2, 4% O_2, and 10% H_2O, with nitrogen as diluent. It was assumed that SO_2 is oxidized to SO_3 prior to sorption, so these uptakes were calculated as grams of SO_3 adsorbed divided by weight of sorbent.

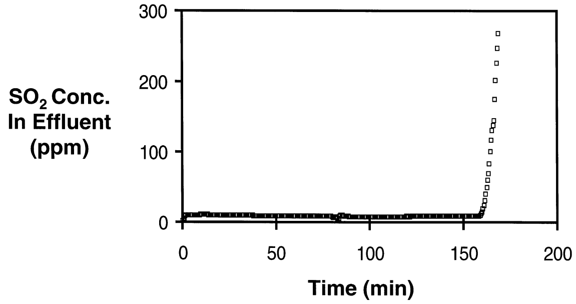

Fig. 1. Typical SO_2 concentration profile during adsorption. Conditions: 1200°F, 3500 GHSV; feed =1% SO_2, 4% O_2, 10% H_2O, balance nitrogen.

Utilizing these conditions, catalyst sulfation was terminated when the effluent SO_2 concentration exceeded 250 ppmv. A typical SO_2 concentration profile during adsorption is shown in Fig. 1. As indicated by the data set, the effluent SO_2 level is extremely low during the adsorption cycle, followed by a very sharp breakthrough front — under these conditions for high-capacity sorbents (vide infra), SO_2 levels <2 ppmw are noted for the first 160 min of the run, followed by an increase to well over 250 ppmw over the course of the last few minutes. Clearly, bypassing is negligible in this system. Further, the shape of this curve is consistent with a bandwise sorption process.

Measured SO_x uptakes utilizing the procedure described above are listed in Table 1. The entries in Table 1 illustrate two critical factors in catalyst selection — that both, effective oxidation promoters and a high-capacity basic sorption site, such as magnesium oxide based sites in magnesium aluminate spinel, are essential for high SO_x uptake capacity. Comparing entries 2, 3, and 4 illustrate that, with ceria as oxidation promoter, SO_x uptake increases with magnesium content — from 7 wt% uptake for CeO_2/Al_2O_3, to 20% for $CeO_2/MgAl_2O_4$ and 25% for $CeO_2/Mg_2Al_2O_5$. Likewise, comparing entries 4, 6, and 7 illustrate that utilizing the same magnesium aluminate spinel base,

Table 1
SO_2 Sorption results[a]

Sorbent	Conditions	SO_x uptake (Wt. %)
$Mg_2Al_2O_5$	Standard	5.0
CeO_2/Al_2O_3	Standard	6.6
$CeO_2/MgAl_2O_4$	Standard	20.4
$CeO_2/Mg_2Al_2O_5$	Standard	25.2
$CeO_2/Mg_2Al_2O_5$	1100°F	14.3
100 ppm $Pt/Mg_2Al_2O_5$	Standard	33.6
$V_2O_5/CeO_2/Mg_2Al_2O_5$	Standard	40.7
$V_2O_5/CeO_2/Mg_2Al_2O_5$	2% SO_2, 1800 GHSV	46.4
High Surface Area $V_2O_5/CeO_2/Mg_2Al_2O_5$	Standard	54.0

[a] Conditions: 1200°F; 3500 GHSV; 4% O_2;1% SO_2; except as noted.

more effective oxidation promoters, such as platinum and combinations of vanadia and ceria, are more effective than ceria alone. Thus, while 25 wt% uptake is measured for $CeO_2/Mg_2Al_2O_5$, uptakes of 34 and 41 wt% are measured for 100 ppm $Pt/Mg_2Al_2O_5$ and $V_2O_5/CeO_2/Mg_2Al_2O_5$, respectively, which may be more effective SO_2 oxidation promoters than ceria alone. As entry 1 illustrates, the lack of an oxidation promoter leads to very low SO_x uptakes — only 5 wt% uptake is noted for $Mg_2Al_2O_5$.

2.2. *Oxidative SO_x capture — reaction chemistry and catalyst characterization*

Understanding the reaction chemistry for the adsorption step is based on both, characterization results and discussions as to the functioning of FCC SO_x transfer additives. In Section 2.1, we have demonstrated that both effective oxidation promoters and a high-capacity basic site are essential for high SO_x uptake capacity. Given these observations, we propose the following reactions (Scheme 2) as critical to effective SO_x uptake.

Scheme 2 incorporates several key elements. First, reactions (1) and (2) illustrate the combustion of H_2S, and other contaminants, such as COS, CO, and CS_2. Reaction (3) is reversible — under the conditions of our study, thermodynamic equilibrium limits the conversion of SO_2 to ca. 50%. Reaction (4) requires a basic metal oxide site capable of forming a stable metal sulfate under these conditions. These considerations underscore the necessity of effective oxidation promoters for effective functioning, since the rate of reaction (3) must be much faster than that of reaction (4) for the bandwise sorption noted above.

– Combustion (Promoted by Ce,V,Pt)

$$2H_2S + 3O_2 \longrightarrow 2\,SO_2 + 2H_2O \tag{1}$$

$$\left[SO_2, COS, CO, CS_2\right] + O_2 \longrightarrow SO_x + CO_2 + H_2O \tag{2}$$

$$SO_2 + 1/2\,O_2 \longleftrightarrow SO_3 \tag{3}$$

$-SO_X$ capture (M = basic metal oxide site)

$$SO_3 + M\text{-}O \longrightarrow M\text{-}SO_4 \tag{4}$$

Scheme 2. Oxidative sorption of sulfur containing species.

Scheme 2 is also consistent with that proposed by Hirschberg and Bertolacini [4] for the effective functioning of SO_x transfer additives. In this scheme, the catalyst adsorbs SO_x under oxidizing conditions in the FCC regenerator and releases it as H_2S in the riser reactor, which is a reducing environment. This proposal is also consistent with Bhattacharyya et. al. [5], and Yoo et. al. [6,7], who discuss the use of ceria-containing magnesium aluminate spinels as advanced catalysts for FCC SO_x transfer applications. In the latter work, it is reported that incorporation of iron, vanadia, and chromium, as a solid solution in the spinel, can aid in the reduction of the sulfated catalyst.

Catalyst characterization results of the fresh and sulfated sorbent help in understanding the chemical transformations occurring during the oxidative sorption step. Detailed characterization results will be presented in a publication to be issued shortly, however, it suffices here to present results germane to the above discussion. XPS results are presented below (see Table 2). Comparison of the sulfur 2*p* binding

Table 2
XPS Characterization of fresh and sulfated sorbent

Material	Mg $2p^a$	Al $2p^a$	S $2p^a$
Sorbent	49.7	74.0	170.0
Sulfated sorbent	50.1	74.2	169.1
$MgSO_4$	50.5	–	169.0
$Al_2(SO_4)_3$	–	75.5	169.3

[a] Binding energies are in eV.

energy of the sulfated sorbent (169.1 eV) to the reference compounds of the fresh oxide (170.0) and $MgSO_4$ (169.0) are consistent with formation of a metal sulfate. Comparison of the Mg 2*p* binding energies for the sorbent, the sorbent following sulfation and $MgSO_4$ is consistent with the formation of some type of sulfated magnesium species, while the data for the Al 2*p* binding energies for the analogous compounds is inconsistent with the formation of a sulfated aluminum species. Infrared characterization finds characteristic sulfate stretches in the 1300–850 cm^{-1} range, and a similarity of the IR spectrum to that of magnesium sulfate. Taken together, these results are consistent with reversible sulfation of magnesium oxide-based sites on the spinel sorbent. Assuming then that the magnesium oxide sites are sulfated, we can calculate that the 54 wt% SO_3 uptake noted in Table 1 is consistent with sulfation of 71% of the available magnesium oxide sites on the $Mg_2Al_2O_5$ base. It is clearly advantageous to have a relatively large number of accessible, basic sites for sorption.

2.3. *Catalyst regeneration: reductive desorption of sulfur species*

Regeneration of the sulfated sorbent may be accomplished with several reducing gases, including hydrogen, carbon monoxide, hydrocarbons, such as propane, and hydrogen sulfide as illustrated in Fig. 2. The reducing gas of choice will depend on price and availability for particular operating scenarios. Below, we focus on reductive desorption of sulfur species using hydrogen as reductant. In this discussion and accompanying thermodynamic calculations, we assume that the sulfated catalyst can be modeled by magnesium sulfate, consistent with the characterization results presented here.

The reduction step can yield SO_2, S_n ($n = 1$–8), or H_2S as the sulfur-containing products of desorption.

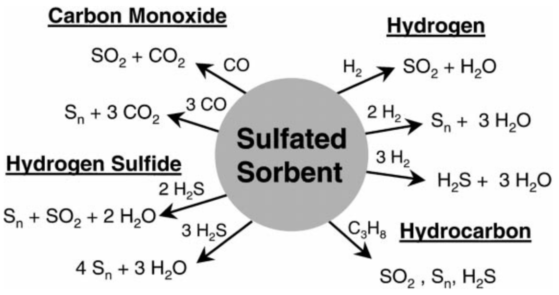

Fig. 2. Sulfur species released open reductive desorption from sulfated most catalyst.

At 1200°F, SO_2 is formed in large excess of S_n or H_2S, with a typical product split of 80% SO_2, 10% S_n, and 10% H_2S. In addition to quantifying the product split obtained upon desorption, the heat of hydrogen reduction was also measured in a adiabatic reaction study and calorimetrically via DSC. The measured heat of reduction at 1200°F is +11 kcal/gmol S, and becomes more exothermic at lower temperatures — at 1050°F, the heat of hydrogen reduction is ca. −5 kcal/gmol S, while the reduction is thermoneutral at ≈1075°F. These observations can be understood by an examination of the reactions leading to these sulfur products, listed as reactions 5–7 below. Thus, formation of SO_2 as the primary desorption product would be endothermic, desorption of H_2S as the primary desorption product would be exothermic, while desorption of S_n would be closer to thermoneutral. Utilizing the 80/10/10 product split mentioned above leads to a calculated heat of reaction of +12 kcal/gmol S at 1200°F, which is in excellent agreement with the measured heat of reaction of +11 kcal/gmol S.

Reaction	ΔH (kcal/gmol S)	
$MgSO_4 + H_2 \rightarrow MgO + SO_2 + H_2O$	+26	(5)
$MgSO_4 + 3H_2 \rightarrow MgO + 1/2\ S_2 + 3H_2O$	−6	(6)
$MgSO_4 + 4H_2 \rightarrow MgO + H_2S + 3H_2O$	−28	(7)

In light of reactions (5)–(7), the reaction chemistry which occurs during the desorption step can be better understood by examining a DSC trace, shown below (Fig. 3). The desorption step is endothermic during the first two-thirds of reduction, and becomes exothermic toward the end of the regeneration. That the last part of the regeneration is exothermic is consistent with

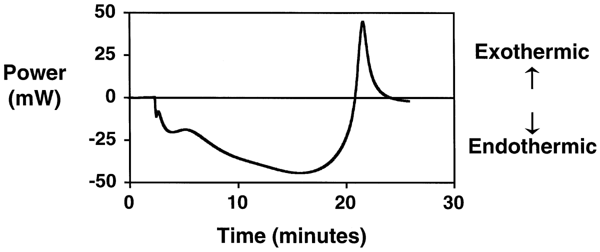

Fig. 3. Heat released during hydrogen reduction of sulfated sorbent as a function of time, as measured by differential scanning calorimetry.

liberation of primarily H_2S, while the endothermicity observed during the initial state of regeneration is consistent with liberation of primarily SO_2. Thus, we can propose that the reaction network is one where the primary product of hydrogen reduction is H_2S. The H_2S thus formed reacts further with sulfated sorbent to desorb S_n and H_2S.

2.4. The MOST process

We have described in some detail the chemistry involved in, and the catalyst selection for, the oxidative sorption of sulfur species onto a promoted magnesium aluminate spinel, and the hydrogen regeneration to liberate sulfur species and regenerate the metal oxide catalyst. Here, we outline how these two steps are used to construct the MOST process in toto.

As outlined above, conditions chosen for the oxidative sorption step are 1000–1400°F, with 1200°F being the preferred temperature. Streams suitable for treatment include those containing mainly SO_2 and H_2S, and also CS_2, COS and CO. The SO_x sorption is band-wise, indicating that the limits as to throughput and SO_2 concentration can be higher than the 3500 GHSV and 1% SO_2 demonstrated in this contribution. Regeneration was also discussed, and is possible with a variety of reducing gases including hydrogen.

The overall process can be operated in fixed swing-bed reactors, a fluid-bed reactor, or moving beds. A process-flow diagram for fixed swing-bed reactors is shown in Fig. 4. H_2S laden streams, such as amine treated acid gas and sour water stripper effluent enter the Claus plant along with air. Most of the sulfur is recovered in the liquid form. The tailgas goes to a burner, where the remaining H_2S is oxidized to SO_2 and SO_3. Excess air is used, such that the burner effluent contains 1–4% O_2. The burner effluent is shown going to sorbent Bed A, where the SO_x is adsorbed. The tailgas then proceeds to the stack for atmospheric release. The regeneration gas circuit is also shown in Fig. 4. Reducing gas, diluted with steam, flows through Bed B, to desorb the sulfur as a concentrated stream of H_2S and SO_2, which is fed back to the Claus unit. At the end of the

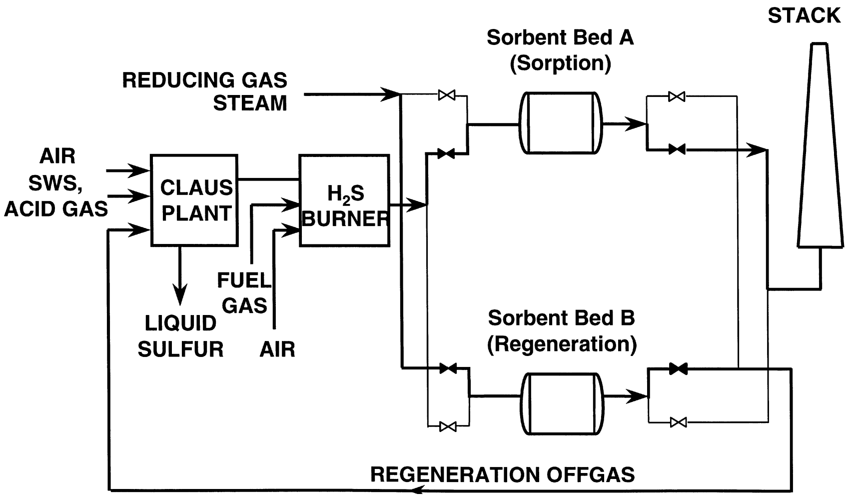

Fig. 4. MOST process flow diagram.

cycle, Bed A is loaded with sulfur, while Bed B had its sulfur removed. At this point, valve positions are changed, causing the tailgas to flow through Bed B, and regeneration gas to flow through Bed A.

Sorbent performance over multiple cycles was also investigated. Utilizing a reactor setup to simulate the process as described above, catalyst was cycled between the oxidative sorption and reductive regeneration modes for many cycles. At the start of this experiment, the SO_x uptake was 58 wt%, and following 210 cycles, the uptake was 42 wt%, which is commercially acceptable. This is equivalent to roughly eight months time-on-stream.

The Shell Flue Gas Desulfurization (SFGD) process [8] functions in a similar manner to the MOST process. The SFGD process is a dry sorbent-based process for flue gas SO_x removal in which SO_2 is oxidatively sorbed onto a copper-on-alumina acceptor to copper sulfate, and is reductively desorbed with hydrogen to net mainly elemental copper and sulfur dioxide. SO_x loadings on this catalyst, however, appear to be significantly lower (<15%), a distinct disadvantage as compared to the MOST process.

The regenerable SO_x sorbents discussed here, which also have CO and H_2S oxidation capability, may be used in applications other than Claus tailgas treatment. For example, a fixed-bed downstream of an FCC regenerator might allow better SO_x capture than the current practice of circulating the sorbent with the FCC catalyst. If an SO_x sorbent bed was used to treat the flue gas from an oil or coal combustor, both SO_x and NO_x emissions could be reduced. The sorbent bed would serve to oxidize CO in the flue gas, so the combustor could be run with less excess air and, hence, lower NO_x make. Because of its simplicity, a solid, regenerable sorbent/oxidizer may have use in numerous other applications.

3. Conclusions

In this contribution, we present a novel process/catalyst combination for reducing tailgas SO_x and H_2S emissions to very low levels (1–5 ppmw). The Mobil Oil SO_x Treatment Process (MOST) consists of the following steps:

1. combustion of tailgas sulfur species to convert all sulfur species to SO_2/SO_3;
2. adsorption of SO_x onto a high-capacity sorbent; and
3. in a separate step, reductive desorption of the sulfur as a concentrated stream of mainly SO_2 and H_2S.

The MOST Process utilizes a regenerable promoted spinel-based sorbent with very high SO_x uptake capacities (>50 wt%), and is both robust and operationally simple.

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