Hybrid Sulfur Recovery Process for Natural Gas Upgrading Quarterly Technical Report

Reporting Period Start Date: 1/1/01
Reporting Period End Date: 3/31/01

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May 2001

DOE No. DE-FC26-99FT40725

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ABSTRACT

This first quarter report of 2001 describes progress on a project funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H_2S in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H_2S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane and other hydrocarbons without oxidation of the hydrocarbons.

The project involves the development of a catalyst using laboratory/bench-scale catalyst testing, and then demonstration of the catalyst at CrystaTech's pilot plant in west Texas. During this reporting periods new catalyst formulations were tested. The experiments showed that the newest catalyst has slightly better performance, but catalyst TDA#2 is still superior overall for use with the hybrid CrystaSulf process due to lower costs. Plans for catalyst pelletization and continued testing are described.

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1.0 INTRODUCTION

This quarterly report is the first technical report for DOE Contract No. DE-FC26-99FT40725 entitled “Hybrid Sulfur Recovery Process for Natural Gas Upgrading” following novation of the project from URS Corporation to CrystaTech, Inc. The CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H₂S) from gas streams and converts it into elemental sulfur. The hybrid CrystaSulf process uses a catalyst to first oxidize about 1/3 of the H₂S to SO₂.

The work described in this report was primarily conducted by CrystaTech's subcontractor TDA Research, Inc., which developed the patented catalysts.

This report is divided into the following sections:

- Section 1 – Introduction
- Section 2 – Executive Summary
- Section 3 – Experimental
- Section 4 – Results and Discussion
- Section 5 – Conclusions

2.0 EXECUTIVE SUMMARY

This project was funded by the U.S. Department of Energy (DOE) to test a hybrid sulfur recovery process for natural gas upgrading. The process concept represents a low cost option for direct treatment of natural gas streams to remove H_2S , in quantities equivalent to 0.2-25 metric tons (LT) of sulfur per day. This process is projected to have lower capital and operating costs than the competing technologies, amine/aqueous iron liquid redox and amine/Claus/tail gas treating, and have a smaller plant footprint, making it well suited to both on-shore and offshore applications.

CrystaSulfSM (service mark of Gas Research Institute) is a new nonaqueous sulfur recovery process that removes hydrogen sulfide (H_2S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes, but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid process, approximately 1/3 of the total H_2S in the natural gas is first oxidized to SO_2 at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H_2S can be oxidized in the presence of methane while avoiding methane oxidation.

The project involves the development of a catalyst using laboratory/bench-scale catalyst testing, and then demonstration of the catalyst at CrystaTech's pilot plant in west Texas. During this reporting periods new catalyst formulations were tested. The experiments showed that the newest catalyst has slightly better performance, but catalyst TDA#2 is still superior overall for use with the hybrid CrystaSulf process due to lower costs. Plans for catalyst pelletization and continued testing are described.

Previous results from this study showed that the hybrid CrystaSulf process is a viable process for treating natural gas. Calculations indicated that natural gas streams containing a fairly wide range of H_2S concentrations and pressures of interest (i.e., pressure up to 6.89 MPa (1000 psi)) could be processed by the hybrid CrystaSulf process. TDA's modified catalysts, especially TDA#2, exhibit high H_2S conversion (99+%) with essentially no slip of oxygen. Changing the formulation, temperature, and $\text{O}_2/\text{H}_2\text{S}$ ratio can be used to control SO_2 selectivity over these catalysts. Further investigation for this promising process is planned.

3.0 EXPERIMENTAL

3.1 Task 1 – Develop a Bench-Scale, Prototype Process to Remove H₂S from Low-Quality Natural Gas

This task had been essentially completed at the time the proposal was submitted on 9 August 1999, and the process was described in the proposal. The following section describes the process and the plan developed to scale-up the application.

3.2 Task 2 – Develop a Detailed Plan for Laboratory/Bench Scale-up Application of the Task 1 Process for Both On-shore and Offshore Applications; Provide a Detailed Engineering Laboratory/Bench Scale-up Application Plan

Background

CrystaSulfSM is a new *nonaqueous* sulfur recovery process that removes H₂S from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes but differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. In the hybrid CrystaSulf process, approximately 1/3 of the total H₂S in the natural gas is first oxidized to SO₂ at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H₂S can be oxidized in the presence of methane (CH₄) while avoiding CH₄ oxidation. In contrast, thermal oxidation would consume valuable natural gas.

In the hybrid CrystaSulfTM process, approximately 1/3 of the total H₂S in the natural gas is first oxidized to SO₂ at low temperatures over a heterogeneous catalyst. Low temperature oxidation is done so that the H₂S can be oxidized directly in the natural gas stream while avoiding hydrocarbon oxidation. H₂S does not have to be separated from the gas stream for sulfur recovery. A little more than 1/3 of the total flow of natural gas to be processed flows over the partial oxidation catalyst in a fixed bed catalytic reactor. The reactor is operated at about 300 psig and 250°C.

About 95% of the H₂S is converted into SO₂ + H₂O and the remaining 5% of the H₂S is converted into S + H₂O. The elemental sulfur is condensed and collected, and the product gas from the reactor (which now contains SO₂) is blended back into the main flow stream. By controlling the splitting ratio to the catalytic reactor, the blended stream will contain the correct proportions of H₂S and SO₂ for removal of the remaining sulfur using the CrystaSulfTM process. A flow diagram of the hybrid CrystaSulfTM process is shown in Figure 1.

The main reactions that take place over the catalyst are the direct oxidation of H_2S into SO_2 (Equation 1), the partial oxidation of H_2S into elemental sulfur (Equation 2), and the Claus reaction between H_2S and SO_2 to produce sulfur (Equation 3). The CrystaSulfSM process runs the Claus reaction in the liquid phase. The objective of the TDA catalytic process is to oxidize approximately 1/3 of the H_2S in the natural gas stream into SO_2 via Equation 1 so that the proper H_2S to SO_2 ratio is present in the natural gas when it enters the CrystaSulfSM process.

The exact amount of gas sent to the catalytic reactor depends on how much elemental sulfur is recovered directly in the partial oxidation. The more sulfur is recovered from the catalytic step, the greater the proportion of gas flow must be sent to the reactor. However, the more sulfur is recovered from the catalytic reactor, the lower the sulfur load on the CrystaSulfSM process. Thus, there is a trade off between the capital and operating costs between the fixed bed reactor and the absorber. The optimum operating conditions depend on the activity of the solid catalyst and its selectivities to SO_2 and elemental sulfur.

Figure 1. Flow diagram for hybrid CrystaSulfSM process.

Equation 1. Total H_2S oxidation.

Equation 2. Partial oxidation of H_2S .

Equation 3. Claus equilibrium.

Requirements of Catalyst used to Oxidize H_2S to SO_2 .

The general requirements for a successful catalyst for the hybrid CrystaSulfTM process are that the catalyst:

1. Exhibit no activity for hydrocarbon oxidation.
2. Give high conversions for H_2S oxidation (lowers the catalyst bed volume).
3. Exhibits high selectivity for SO_2
4. Selectivity to sulfur is a bonus.
5. All elemental sulfur formed needs to remain in the vapor phase in the reactor (i.e. the operating temperature of the catalyst must be above the sulfur dew point).

4.0 RESULTS AND DISCUSSION

We have tested three promoted versions of our partial oxidation catalyst that is based on Mo, Nb, and TiO_2 . In the first catalyst (designated TDA#1) a transition metal was added that is known to improve the selectivity of the catalyst for SO_2 at the expense of forming elemental sulfur. In the second catalyst (TDA#2) a different transition metal was added that is even more active for total H_2S oxidation, and as expected, more SO_2 was formed over this second catalyst. The third promoter (found in TDA #3) is somewhat better than that used in TDA #2. The results for these tests of TDA #1 and TDA #2 were reported earlier. In this report we discuss a third catalyst (TDA #3) that is even more selective for SO_2 production.

4.1 Testing of TDA#3 Catalyst

Table 1 shows the experimental conditions for testing the TDA #3 catalyst. All of the experiments were done with the catalyst at a temperature of 250°C and the pressure equal to 300 psig (312 psia). The space velocity was $3350 \text{ cm}^3_{\text{gas}}/\text{cm}^3_{\text{catalyst}}/\text{hr}$. Water vapor was added that was equivalent to the dew point pressure at 100°F (0.95 psi). This corresponds to a mole fraction of 0.3% at 312 psia. The barometric pressure at TDA (located near Denver, CO is approximately 12.2 psia). The inlet H_2S concentration in all cases was 2000 ppm, and the feed gas contained 10% methane. The experiments were done at two concentrations of oxygen, 2000 ppm ($\text{O}_2/\text{H}_2\text{S} = 1$) and 3000 ppm ($\text{O}_2/\text{H}_2\text{S} = 1.5$). The balance gas was N_2 .

Table 1. Experimental conditions for TDA #3 catalyst

Parameter	Value
H_2S	2000 ppm
O_2	2000 & 3000 ppm
N_2	Balance
CH_4	10 vol %
Temperature	250°C
Pressure	300 psig
Humidity	Sat. at 100°F

Figure 2. Experimental run with TDA#3, O_2 to H_2S ratio = 1.5.

Experimental results when H_2S to O_2 ratio = 1.5

Figure 2 shows the results for TDA catalyst #3 run when the O_2/H_2S ratio = 1.5. The feed contained 2000 ppm H_2S , 3000 ppm O_2 approximately 0.3 vol% H_2O (3000 ppm) and 10% CH_4 , with the balance being N_2 . The experiment was run for approximately 20 hours at $T = 250^\circ C$ and $P = 312$ psia. The H_2S conversion was 100% during the entire experiment. At the beginning of the experiment the selectivity for sulfur was almost 90% with very little SO_2 being formed. Gradually, over the next 10 hours the selectivities shifted to approximately 10% for sulfur and 90% for SO_2 . By 20 hours, the SO_2 selectivity slowly increased to 94% (6% elemental sulfur) Because the H_2S conversion was 100%, the yields of sulfur and SO_2 are numerically equal to their selectivities.

Experimental results when H_2S to O_2 ratio = 1.0

The same charge of TDA #3 catalyst was then tested at a O_2/H_2S ratio of 1. The results are shown in Figure 3. Note that the induction time is much shorter in Figure 3 compared to Figure 2. This is due to the fact that fresh catalyst (still in the oxide form) was used for the experiment shown in Figure 2 whereas we used the tested catalyst for the experiment with $O_2/H_2S = 1.0$. As a result, some of the induction time in Figure 2 is undoubtedly due to conversion of the oxide components in the catalyst to steady state concentrations of sulfide (with possibly chemisorbed sulfite/sulfate because of the presence of oxygen in the feed). The short induction time in Figure 3 is probably due to the lag time in switching the flow from the bypass (where we measure the inlet H_2S concentration) to flow over the catalyst. At a pressure of 312 psia, the residence time in the catalyst bed (approximately 1 cm^3 volume) is about 1 second. The total volume of the reactor and all tubing is about 500 cm^3 so there is approximately a 20 minute lag time for several reactor volumes to pass through the system and the concentrations in the gas phase at the GC become equal to those over the catalyst.

Figure 3. Experimental run with TDA#3, O_2 to H_2S ratio = 1.

The selectivity for SO_2 was reduced from 94% when $\text{O}_2/\text{H}_2\text{S} = 1.5$, to 74% (26% S) when $\text{O}_2/\text{H}_2\text{S} = 1.0$. Again because the H_2S conversion was 100%, the selectivities are numerically equal to the yields for SO_2 and elemental sulfur. Reduced selectivity for SO_2 with decreasing $\text{O}_2/\text{H}_2\text{S}$ is consistent with the results obtained earlier with the TDA #2 catalyst.

Figure 4. Experimental run with TDA#3, O_2 to H_2S ratio = 1.

Figure 4 shows the data from the paramagnetic O_2 analyzer during the test of TDA catalyst #3 at a $\text{O}_2/\text{H}_2\text{S}$ ratio = 1.0. The inlet concentration into the reactor was 3000 ppm (0.3%) and the full range of the analyzer is 0 – 5% (hence the noisy signal). The less noisy line is the feedback flow signal from the mass flow controller used to meter in 2.7% O_2/N_2 and shows that O_2 was flowing into the reactor during the experiment.

Figure 5. Rerun of TDA #3 test at $O_2/H_2S = 1.5$

Figure 4 shows that there was no O_2 in the outlet gas so all of the oxygen was being consumed by catalytic reaction. Figure 5 shows the results for rerunning TDA #3 catalyst at 300 psi, $250^\circ C$ and $O_2/H_2S = 1.5$. Because the catalysts was not in the oxide form. There was essentially no induction time during the test shown in Figure 5. As was the case with the first run of TDA #3 shown in Figure 2, the selectivity to SO_2 was quite high (96%) with the selectivity to sulfur being 4%. This is within experimental error of being identical to the performance of fresh TDA #3 catalyst after 20 hours on-stream.

Oxygen mass balance

Because we have no way to directly measure the amount of sulfur produced during the reaction, we rely on the oxygen mass balance to check our assumptions that only two reactions are occurring (Equation 1 and Equation 2). The results from the O_2 analyzer indicated that in all of the runs with TDA #3, all of the O_2 was consumed (outlet concentration of zero).

The concentration of sulfur dioxide is measured during the experiment using the GC and from this value and the known inlet concentration of H_2S and the known H_2S conversion, the conversions to SO_2 (X_{SO_2}) and sulfur (X_S) are calculated. The unknown sulfur vapor concentration $[S]$ can then be calculated using the mass balance equations shown in Figure 6. Finally the amount of O_2 required is calculated and if this is close to the actual inlet concentration of oxygen, then the assumptions in the mass balance are valid and one can conclude that only SO_2 and S are formed.

Figure 6 shows the equations used for calculating the oxygen mass balance. The inlet concentration of H₂S was [H₂S]₀ = 2000 ppm, the inlet concentration of oxygen was [O₂]₀ = 3000 ppm. [O₂]_{req'd} in Figure 6 is the inlet O₂ concentration that would be required to produce all of the SO₂ and S produced during the experiment. The closer this value is to the inlet O₂ concentration used (i.e. [O₂]₀ = 3000 ppm) the better the mass balance for oxygen. The inlet concentrations of SO₂ and S were zero.

$$[\text{H}_2\text{S}]_0 = 2000 \text{ ppm}$$

$$[\text{O}_2]_0 = 3000 \text{ ppm}$$

$$[\text{O}_2]_{\text{outlet}} = 0$$

$$\frac{[\text{H}_2\text{S}]_0 - [\text{H}_2\text{S}]}{[\text{H}_2\text{S}]_0} = X_{\text{H}_2\text{S}}$$

$$\frac{[\text{H}_2\text{S}]_0 - [\text{SO}_2]}{[\text{H}_2\text{S}]_0} = X_{\text{S}}$$

$$[\text{SO}_2] = [\text{H}_2\text{S}]_0 - X_{\text{S}}[\text{H}_2\text{S}]_0$$

For the test of TDA #3 shown in Figure 5, the selectivity to SO₂ was $X_{\text{SO}_2} = 0.95$ (average) and the selectivity to elemental sulfur was $X_{\text{S}} = 0.05$ (average). For an inlet concentration of [H₂S]₀ = 2000 ppm, $X_{\text{SO}_2} = 0.95$ and $X_{\text{S}} = 0.05$, and an SO₂ concentration of 1918.5 ppm, the calculated sulfur vapor concentration is [S] = 81.52 ppm.

$$\frac{[\text{H}_2\text{S}]_0 - [\text{S}]}{[\text{H}_2\text{S}]_0} = X_{\text{SO}_2} = 1 - X_{\text{S}}$$

$$[\text{S}] = [\text{H}_2\text{S}]_0 - X_{\text{SO}_2}[\text{H}_2\text{S}]_0$$

$$[\text{O}_2]_{\text{req'd}} = \frac{3}{2}[\text{SO}_2] + \frac{1}{2}[\text{S}]$$

Figure 6. Equations for oxygen mass balance check.

These concentrations of SO₂ and S require [O₂]_{req'd} = 1.5(1918.5) + 0.5(81.52) = 2919 ppm of O₂. The inlet concentration was [O₂]₀ = 3000 ppm so we can account for 97.3% of the oxygen by forming only SO₂ and S. This degree of accuracy is well within the experimental accuracy of the mass flow controllers and GC analysis of the product gases. Thus, we conclude that with TDA #3 catalyst run at O₂/H₂S = 1.5, only SO₂ and S are formed and no SO₃ is formed. These results are also consistent with our earlier results for the TDA #1 and TDA #2 catalysts where the oxygen mass balance closure was greater than 95% and therefore only SO₂ and S were formed over these catalysts.

We also do not expect much SO₃ based on the descriptions of the industrial synthesis of SO₃ via SO₂ oxidation found in the literature (Stocchi 1990). Sulfur trioxide is used for sulfuric acid manufacture and is made by oxidizing SO₂ with O₂ over V₂O₅ catalysts. The optimum temperature for industrial synthesis, from both a kinetic and thermodynamic standpoint, is between 400°C and 500°C (Stocchi 1990). These temperatures are much higher than we operate our catalyst (250°C) and thus we would expect very poor activity for SO₃ formation. Also, V₂O₅ is a more aggressive oxidation catalyst than our catalysts.

4.2 Comparison between TDA catalysts 1, 2 and 3.

Previously, we reported the results from similar tests for two other catalysts, TDA #1 and TDA #2, that were also promoted versions of TDA's partial oxidation catalyst. Figure 7 shows the results for TDA #1 and Figure 8 shows the results for TDA #2. Figure 7 shows that the average

H₂S conversion was about 70% and the selectivity for SO₂ was about 30% for the TDA #1 catalyst. This corresponds to only 21% yield of SO₂. The selectivity for sulfur was about 70% so the yield of elemental sulfur was only 49%. Because of the rather poor performance of this version of the catalyst, it is no longer under consideration.

Figure 7. Results for TDA #1 catalyst.

The performance of the TDA #2 catalyst was considerably better than catalyst TDA #1, especially when the O₂/H₂S ratio was 1.5. At the higher O₂/H₂S ratio, the H₂S conversion was complete (100%), the selectivity to sulfur was only 8%, and the selectivity to SO₂ was 92%. When the O₂/H₂S ratio was decreased to O₂/H₂S = 1, the H₂S conversion was slightly reduced (98%), the selectivity to SO₂ was 74% and the sulfur selectivity was 29%. These correspond to a SO₂ yield of 73% and a sulfur yield of 28%. The amount of oxygen added (appearing as the O₂/H₂S ratio) is the most sensitive variable that we have found for controlling the selectivity of the catalyst for SO₂ and S. The effect of the O₂/H₂S is greater than the effects of temperature, pressure or space velocity in determining SO₂ yields and we can use the oxygen concentration to control the selectivity to SO₂ to different levels as required by the process.

Figure 8. Results for TDA #2 catalyst.

The performance of the TDA#3 catalyst was virtually the same as the performance of TDA #2 under the conditions where $O_2/H_2S = 1$; however, increasing the O_2/H_2S ratio to 1.5 clearly improved the performance of both catalysts, with TDA # 3 being slightly better. Based on our tests to date, the differences between TDA #2 and TDA #3 are minimal when operated at $O_2/H_2S = 1.5$ (TDA #3 has only a 4% better SO_2/S selectivity). Because the promoter used in TDA #3 is considerably more expensive than the promoter used in TDA #2, we recommend using TDA #2 as the catalyst for testing at larger scales. The results for the three TDA catalysts along with the operating conditions used in each test are given in Table 2.

Table 2. Summary of catalyst test results for TDA #1, 2 and 3.

Catalyst	O_2/H_2S	Temp (°C)	Pressure (psig)	GHSV (h ⁻¹)	H ₂ S conv. (%)	SO ₂ yield (%)	Sulfur yield. (%)
TDA#1	1.0	250	250	1910	70	27	43
TDA #2	1.0	250	300	3350	96	69	27
TDA #2	1.5	250	300	3350	100	92	8.6
TDA #3	1.0	250	300	3350	100	74	26
TDA #3	1.5	250	300	3350	100	94*	6*
TDA #3	1.5	250	300	3350	100	96#	4#

* after 20 hrs (10 hr induction time with fresh TDA #3)

rerun of $O_2/H_2S = 1.5$ with TDA #3 using tested catalyst.

4.3 Combustion of C₂+ hydrocarbons

In all of our catalyst tests we have added 10% methane to the feed and have found that no methane oxidation occurs over our catalysts at T = 250°C and P = 300 psig. Methane is the most

difficult of the hydrocarbons to oxidize (highest activation energy) and in the real gas application (that we will encounter in the pilot plant), C_2 , C_3 and possibly C_4 hydrocarbons will be present. While the concentrations of these hydrocarbons are a few percent each, their combustion is undesirable because this consumes oxygen and reduces the BTU value of the gas.

We are planning to add ethane and propane to our feed to experimentally determine if ethane and propane are oxidized over our catalysts; however, based on the literature in this area, we expect that these hydrocarbons will not be oxidized to a significant extent, especially given our relatively low operating temperature of 250°C.

Several studies have examined the catalytic oxidation of C_2+ hydrocarbons (Gulianti 1999; Hernandez and Ozkan 1990; Ozkan et al. 1990; Udea et al. 1999) and while the main interest of these researchers was to develop partial oxidation catalysts for converting low cost hydrocarbons into value added chemicals (e.g. butanes into maleic anhydride), their observations give us insights as to what to expect for hydrocarbon oxidation (partial or complete) over our catalysts.

The review of supported vanadia catalysts by Gulianti discusses how the nature of the support is important in controlling the selectivity of vanadia catalysts for partial versus total oxidation. For example, when microcrystallites of V_2O_5 are present on the catalyst during the oxidation of butene, the selectivity shifts toward deep oxidation to yield CO_2 . In contrast, when the vanadia is highly dispersed, the selectivity to maleic anhydride is improved. The specific phase of the support and how it is prepared are less important in determining catalyst selectivity and activity than are the molecular structures of the vanadia overlayers (Gulianti 1999).

This effect of monolayer dispersion is likely relevant for other oxide on oxide catalysts such as our catalysts that contain MoO_3 and Nb_2O_5 supported in TiO_2 (with a promoter added for catalysts TDA #1, 2 and 3). At low loadings, MoO_3 and Nb_2O_5 tend to wet the TiO_2 surface forming thin layers. Thin layers of oxides are crystallographically quite different from the bulk oxides and thus can be expected to exhibit different catalytic activities (Kiselev, V.F., and Krylov, O.V. 1989). If the behavior of MoO_3 follows the same pattern as vanadia, then thin MoO_3 layers should be less active for total oxidation than bulk MoO_3 .

The catalysts we use for partial oxidation of H_2S to produce both SO_2 and S are promoted versions of our $MoO_3/Nb_2O_5/TiO_2$ catalyst that we use to produce elemental sulfur in high yields by H_2S partial oxidation. Our catalyst contains MoO_3 which is generally a good oxidation catalyst, and while we expect relatively low hydrocarbon oxidation activity because it is highly dispersed, the literature that discusses MoO_3 as a catalyst for the partial/total oxidation of alkanes and alkenes is useful to examine when attempting to anticipate how the C_2+ components of natural gas will behave in the hybrid CrystaSulf process when H_2S is oxidized to SO_2 over our catalyst.

In the study by Hernandez and Ozkan (1990), the authors prepared two versions of MoO_3 by using different thermal treatments. In one case, the crystallites exhibited an abundance of exposed flat basal (100) planes of MoO_3 and in the other case, there was a higher percentage of the (010) planes exposed. The (010) planes have more coordinatively unsaturated atoms in them than the (100) planes. The authors then examined the oxidation of 1-butene, 1,3-butadiene, furan

and maleic anhydride over these catalysts. The reaction temperatures were between 410°C and 600°C. They found that with the MoO_3 catalysts that had mostly (100) planes exposed, better selectivity for partial oxidation was observed. In contrast, when the catalysts had a higher fraction of $\text{MoO}_3(010)$ planes exposed, more deep oxidation to CO and CO_2 was found. The authors suggested that this was due to sites that break C-C bonds being present on the (010) face and that the (100) has a limited capability to donate oxygen to the adsorbed hydrocarbon. This would be consistent with the accepted thought in catalysis that coordinatively unsaturated sites (on any catalyst) are usually more reactive than sites that have more nearest neighbors. Not infrequently the more active sites produce undesirable side reactions.

The temperatures used in the Hernandez and Ozkan study were considerably higher than our temperature of 250°C. Furthermore, the basal planes of (100) MoO_3 only produced partial oxidation. Thus, even if there were defect sites in the MoO_3 phase in our catalysts (which would have reactivity similar to (010) surface of MoO_3) much higher temperatures than we use appear to be required to obtain significant amounts of hydrocarbon oxidation even on these more energetic surfaces.

In support of our hypothesis that our temperatures are too low to obtain significant C_2+ oxidation over our catalysts, the work of Ozkan et al. (1990) shows that the activity of MoO_3 for the oxidation of 1-butene is modest even at a temperature of 480°C. In that work, the authors compared the activities of CdMoO_4 , $\text{CdMoO}_4/\text{MoO}_3$, and pure MoO_3 in 1-butene oxidation and found that the overall conversion was highest with CdMoO_4 (80%) intermediate with $\text{CdMoO}_4/\text{MoO}_3$ (40%), and lowest with MoO_3 (10%). The catalytic activity for the deep oxidation of 1,3-butadiene to CO_2 (at 480°C) was somewhat larger because the diene is more reactive, but was still only 35% with MoO_3 . Again the high temperatures and the fact that olefins are much more reactive than alkanes, suggests that we will see little if any ethane or propane oxidation with our catalysts at 250°C.

Finally, the work of Ueda et al. (1999) examined the oxidative dehydrogenation of ethane to form ethylene which subsequently oxidized to acetic acid. Their catalyst was a Mo-V-M based oxide ($\text{M} = \text{Al}, \text{Fe}, \text{Cr}$), and as in the other work, the temperature had to be fairly high (340°C) to achieve acceptable rates. This catalyst could also oxidize methane, but the temperature had to be 400°C, again much higher than our temperature. Also, containing Cr and V in significant amounts, their catalyst will be more active total oxidation compared to our promoted Mo-Nb- TiO_2 catalyst.

5.0 CONCLUSIONS

5.1 Summary

We have completed the testing of a third promoted version of our Mo-Nb-TiO₂ based partial oxidation catalyst and found that we get excellent conversion of H₂S into sulfur and SO₂ with selectivities of approximately 4% S and 96% SO₂ when the ratio of oxygen to hydrogen sulfide is O₂/H₂S = 1.5. The feed gas for these reactions was chosen to simulate the real natural gas stream and contained 10% CH₄, water at a 100°F dew point and 2000 ppm of H₂S. The balance of the gas was nitrogen instead of CO₂ to simplify performing the experiment at high pressure. Our previous experience with CO₂ and N₂ with our catalysts indicates that CO₂ is inert so substituting N₂ will not give misleading results. The reactions were run at 300 psig. The only components not added to the feed were ethane and propane. We will add these components in future.

Based on our comparison between catalysts TDA #1, 2 and 3, it appears that the TDA #3 catalyst is best in performance, but considering the marginal improvement compared to TDA #2 and the relative cost of the promoters, TDA #2 is probably the best choice. The operating conditions in either case would be O₂/H₂S = 1.5; P = 300 psig and T = 250°C. Under these conditions the H₂S conversion is 100%, and the selectivity to SO₂ is approximately 96%. However, if lower SO₂ selectivity is desired to increase the amount of sulfur recovered by our oxidation process (to minimize the sulfur load on the CrystaSulf process), the O₂/H₂S could be lowered to closer to unity. Importantly, all three catalysts have been tested for 20+ hours and are quite stable.

5.2 Planned Activities

We will experimentally verify that the ethane and propane are not oxidized over the TDA #2 and #3 catalysts. The first experiment will be to run with 3000 ppm O₂ and the appropriate concentrations of ethane and propane and ensure that no O₂ is consumed. This experiment will be done as a function of temperature and will last for about 20 hours. In the second test we will use a simulated natural gas stream that contains 10% CH₄, 3% C₂H₆ and 2% C₃H₈ with 2000 ppm of H₂S adding 3000 ppm of O₂. The balance of the gas will be nitrogen. If no hydrocarbon oxidation is occurring, then it should be possible to account for all of the oxygen consumed by the formation of SO₂ and S only with the oxygen mass balance discussed above.

Catalyst pellet production

Once we have determined the best catalyst composition, a qualified supplier of the material is needed. The supplier will need to provide reproducible batches for qualification, and ultimately supply the required quantities for pilot plant testing. When commercial quantities of catalysts and sorbents designed by TDA are needed, TDA generally supplies them through Saint Gobain NorPro (Cleveland, OH).

NorPro is one of the Nation's largest suppliers of catalysts and sorbents and is a wholly owned subsidiary of Saint Gobain. NorPro's annual sales exceed \$100 million. NorPro has produced several materials according to recipes provided by TDA. Our first joint effort was the production of ton quantities of ZnO based hot-gas clean up sorbents, and we are currently working with

NorPro to manufacture the catalyst charge for our the demonstration plant for the partial oxidation of hydrogen sulfide to sulfur and water, a plant which will be installed in the coming year at a natural gas processing facility in western Canada.

Saint-Gobain NorPro Corporation (NorPro) is a subsidiary of Saint-Gobain Corporation Inc., which is a subsidiary of Compagnie de Saint-Gobain. Saint-Gobain is one of the 100 leading industrial companies in the world in producing and transforming basic materials, including glass, cast iron, plastics and ceramics. Saint-Gobain has annual sales of around \$23 billion worldwide. NorPro is a leading supplier of distillation and separation equipment, heat storage technology and catalyst carriers and ceramics for the chemical, petrochemical, and petroleum refining industries.

NorPro has three operating groups, specializing in Mass Transfer, Catalytic Products, and Ceramics. The Catalytic Products are used by the chemical and allied processing industries worldwide. The Catalytic Products group produces porous ceramic catalyst carriers in three sites in the U.S., upon which catalytically active materials are absorbed. Control of porosity optimizes the carrier for a particular catalytic reaction.

NorPro produces what is considered to be the industry's largest selection of standard and specialty formulated porous ceramic catalyst carriers in a wide variety of surface areas, porosities, and shapes. NorPro has extensive experience with alumina, titania, silica, and other inorganic materials. The expertise that NorPro has acquired is directly related to the emphasis placed on research and development.

NorPro owns and operates a Research and Development Laboratory located in Stow, Ohio. A significant part of this laboratory is devoted to the development of tailored porous ceramic materials. These materials are produced by mixing, extrusion, shaping, drying and calcination. Other forming methods are also utilized, such as various agglomeration techniques. The equipment available includes full size apparatus for these various stages, in order to virtually eliminate scale up problems. Full scale calcination equipment (tunnel, rotary, and periodic kilns) is available at NorPro's production facilities in Bryan, Texas; Ravenna, Ohio; and Daisy, Tennessee. NorPro maintains a very well equipped analytical laboratory for the chemical and physical measurements that may be required. Relevant equipment available includes the following: Surface Area Analyzers, Micromeritics 2300, Flowsorb Micromeritics 2600, Digisorb Micromeritics 2405 ASAP, Mercury Porosimeters, Quantochrome Autoscan SP-60-3, Quantochrome Autoscan 25, AS-25-1 Amonco-Winslow (0 - 3,000 lb), Flat Plate Crush Strength Gauges, Comten 945 KVC0300 (to 5,000 lb), and Comten 50-02 (to 600 lb). In addition, a wide range of other analytical instrumentations is available, including: X-Ray Diffraction, Scanning Electron Microscopy (with Energy Dispersive Spectroscopy), Thermogravimetry (DTA, TGA, TMA), Particle size analysis Atomic Absorption (with graphite furnace), Sulfur analysis, X-Ray Florescence (XRF) and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP AES).

TDA will provide the catalyst formulations to Norpro and will have them manufacture batches of pellet catalysts for testing at TDA. Following the testing, NorPro will scale up the catalyst manufacture in collaboration with TDA.

Durability testing

TDA will perform a catalyst lifetime/durability test on the pelletized form of the catalyst using their pellet reactor. Our pellet reactor is designed specifically to be able to test catalysts in the final physical form (e.g. 0.1-0.3 inch pellets) that will be used in the pilot plant. This testing ensures that no unforeseen variations in catalyst performance are introduced when the catalyst is manufactured in its final physical form.

6.0 REFERENCES

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