



Shedding Light on the Facile Conversion of CS₂ across Claus Tail Gas Hydrogenation Catalysts

Christopher B. Lavery, Dao Li, Ruohong Sui, and Robert A. Marriott

Alberta Sulphur Research Ltd.

Contacts: rob.marriott@ucalgary.ca, cblavery@ucalgary.ca

Abstract

Inferred CS₂ hydrolysis rates across tail gas treatment unit (TGTU) hydrogenation reactors, after accounting for CH₃SH and CH₄ formed via hydrogenation, are higher than predicted from established Claus kinetics. This discrepancy led us to investigate the roles of the catalyst support, the deposited CoMo species, and potential direct reaction with SO₂ under TGTU-relevant conditions. Our findings show that when sulfate accumulation is minimized and SO₂ is effectively taken to extinction, the inherent hydrolysis activity of Al₂O₃ can more fully be exploited. Direct CS₂ + SO₂ reaction was negligible with any minor activity likely attributable to residual surface H₂O and H₂S, rather than an independent reaction pathway. Although the catalyst was prepared in-house and absolute product distributions may differ from commercial catalysts, the observed trends and internal comparisons are expected to hold true. These findings help rationalize the consistently high CS₂ conversion observed in TGTUs and offer valuable inputs for kinetic modeling. It should be noted that this study did not examine CoMo supported on TiO₂, which is intrinsically less susceptible to sulfate buildup and has been shown to offer other advantages as well through easier activation (*i.e.*, sulfiding / reduction).

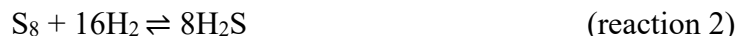
Introduction

Sulfur recovery from H₂S within the thermal and catalytic stages of the modified Claus process is equilibrium limited at *ca.* 98%.^[1] As such, there is still *ca.* 1% H₂S, 0.5 % SO₂, and hundreds to thousands parts per million by volume (ppmv) of COS and CS₂ in a typical Claus tail gas.^[2, 3] These residual sulfur compounds are often treated by use of a tail gas treatment unit (TGTU), where SO₂, COS, CS₂, and S₈ vapour are converted to H₂S which is then captured by low-pressure H₂S-selective amine and recycled back into the modified Claus process to achieve a sulfur recovery of >99.9%.^[4] The off-gas from the tail gas amine, containing very small levels of sulfur species, is then sent to a final thermal oxidizer unit before it is emitted to the atmosphere in the form of SO₂.

The chemistry that occurs across the TGTU hydrogenation reactor is complex and interconnected.^[4-8] The active form of the catalyst consists of CoS and MoS₂ deposited on either an Al₂O₃ or TiO₂ support, and both the deposited CoMo and support material play a crucial role in facilitating the necessary transformations. Note that the hydrogenation active sites are located at the edges of the molybdenum slabs and the primary role of the cobalt is to prevent sintering and agglomeration.^[8-13] Some relevant hydrogenation reactions involving sulfur are shown in reactions 1-4. Reactions 1 and 2 simply show the reduction of SO₂ and elemental sulfur to H₂S but some ASRL laboratory results suggest at least some of the SO₂ may take part in the Claus reaction to



form elemental sulfur first.^[14] Reactions 3 and 4 show the hydrogenation of CS₂ to CH₄ proceeding through a CH₃SH which can often be detected, particularly at lower temperatures.



The conversion of CO also occurs at the same active sites as reactions 1-4 and is crucial for promoting the high sulfur recoveries associated with reductive / amine based TGTU technologies. Ideally, CO is converted to CO₂ and active surface bound hydrogen by the water gas shift reaction (reaction 5). However, as a tail gas catalyst ages, the water gas shift reaction is the first to suffer which allows for more CO to take part in other undesirable chemistry. Indeed, a loss in water gas shift reaction activity can manifest in increased COS concentrations from the sour gas shift reaction (reaction 6) or by direct combination of CO with sulfur (reaction 7).^[7]



The hydrolysis of COS (reaction 8), either residual from the Claus converters or formed from reactions 6 and 7, takes place on the catalyst support. Note reaction 8 is equilibrium limited and, as such, some trace COS will always persist. Conversely, the hydrolysis of CS₂ (reaction 9) on the catalyst support has no thermodynamic limitation and, in theory, can proceed to completion.



However, based on data collected under Claus converter conditions, the hydrolysis of CS₂ should be severely kinetically limited (chemical) at TGTU temperatures, particularly when the bed inlet is restrained to 220-240°C (430-465°F) by use of indirect steam reheaters.^[15] Herein lies the contradiction that the present work seeks to address. Even in low-temperature TGTU applications, the conversion of CS₂ across the hydrogenation reactor is typically quantitative. And after accounting for CS₂ conversion via hydrogenation, evidenced by the formation of CH₃SH and CH₄, the residual fraction, assignable to hydrolysis, appears significantly greater than what previously established kinetic parameters predict.^[15] Of course, the catalyst surface speciation will be different when comparing the Claus catalyst beds to the TGTU hydrogenation reactor. Of particular consequence here is the relative amounts of sulfate, an unavoidable intermediate in the Claus reaction. Indeed, ASRL, and others, have shown the detrimental effect that surface sulfate, dictated by temperature and H₂S to SO₂ ratio, has on CS₂ hydrolysis activity.^[16-18] In the TGTU



hydrogenation reactor, where Claus equilibrium conditions are not met, the catalyst surface diverges from that of a Claus converter: the accumulation of surface sulfate intermediates is suppressed and SO₂ is reacted to extinction. Thus, while employing a CoMo on Al₂O₃ catalyst that was prepared in-house, this difference in sulfate coverage was identified as a key factor to be examined in rationalizing the unexpectedly high CS₂ hydrolysis observed across the hydrogenation reactor.

The reaction of CS₂ with SO₂ (reaction 10) across Claus Al₂O₃ and TiO₂ was investigated by ASRL over 20 years ago.^[19] The reaction products here would be CO₂ and elemental sulfur, which under TGTU conditions, would be further reduced to H₂S, making it difficult to decipher from the hydrolysis pathway under normal operating conditions. Our previous work in this area concluded that reaction 10 is not likely a significant to the overall CS₂ conversion across Al₂O₃ under Claus conditions. In the current study, we also revisited this chemistry to evaluate if the molybdenum active sites present on a tail gas catalyst provide enhanced conversion via reaction 10.



Experimental

Impregnation of CoMo on the catalyst support

In a typical synthesis, 7.5 g of (NH₄)₆Mo₇O₂₄·4H₂O (corresponding to 16.2 wt% MoO₃ in the final product) was dissolved in 30.0 g of deionized water (solution A) at room temperature. Separately, 5.5 g of Co(NO₃)₂·6H₂O (3.8 wt% CoO in the final product) was dissolved in 10.0 g of deionized water (solution B). The transparent solutions A and B (A was colorless and B was dark red) were added to 40.0 g of Al₂O₃ in a 200 mL beaker, one immediately after the other, under constant stirring with a glass rod. Several mL of excess liquid (pink solution) remained in the beaker along with the wet catalyst support. The resulting mixture was placed in the oven at 50°C (122°F) without agitation for 10 h, and then placed under vacuum at 80°C (176°F) for 8 h and calcined at 400°C (752°F) in air for 2 h. The Al₂O₃ support material was a commercial product that was provided in-kind to ASRL.

Sulfiding/Reduction of the CoMo on Al₂O₃ catalyst

Sulfiding of the CoMo on Al₂O₃ catalyst was performed according to a procedure adapted from industry. This involved purging the catalyst with dry, O₂-free N₂ for *ca.* 16 h (overnight) and then raising the temperature of the bed to 200°C (392°F). At a gas hourly space velocity (GHSV) of 1250 h⁻¹ (NTP), a sulfiding stream consisting of 2.5% H₂S, 10.0% H₂ and 87.5% N₂ was then introduced, and the temperature of the catalyst was slowly raised to 320°C (608°F) at an average rate of 15°C·h⁻¹. Following this 8 h temperature ramp, the catalyst was held at 320°C (608°F) for a further 4 h. After the 4 h temperature soak, the sulfiding stream was shut off and replaced by dry, O₂-free N₂ while adjusting the catalyst bed to the appropriate experimental temperature. Figure 1 shows time-lapsed data of product H₂S and observed experimental temperatures. As can be seen, product H₂S, denoted as [H₂S]_p had approached feed H₂S, denoted as [H₂S]_f, by the end of the 4 h temperature soak, indicating that the bulk of the sulfiding was complete. For producing a fully



activated tail gas catalyst catalyst, the importance of i) conversion of CoMo from the oxide to the sulfide form, ii) reduction of Mo from a +VI to a +IV oxidation state, and iii) assembly of MoS₂ into crystalline slabs has been discussed previously.^[8-13]

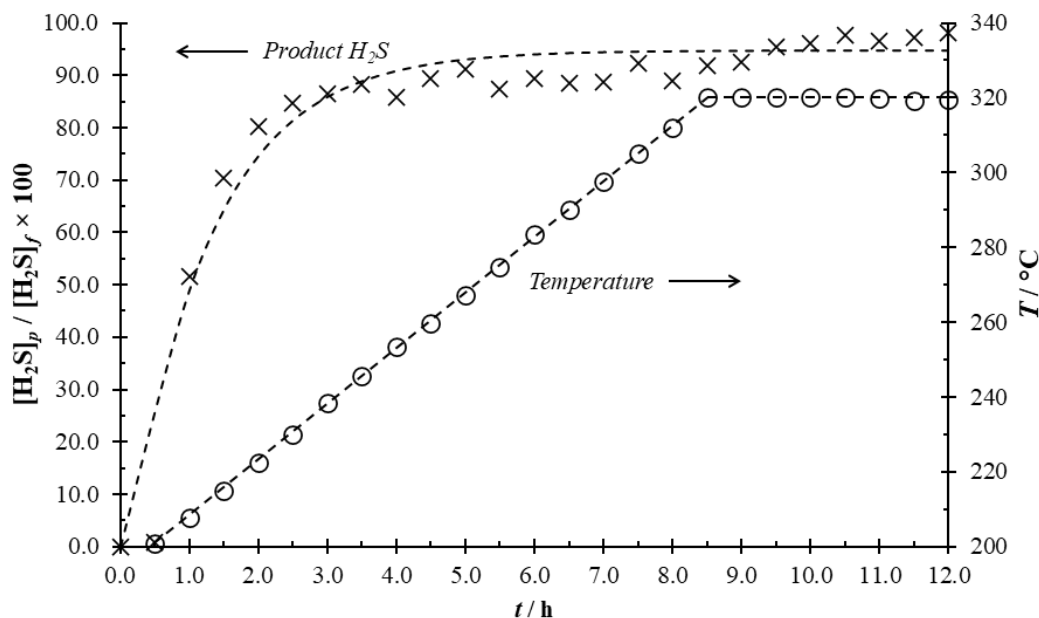


Figure 1. Plot of product H₂S and temperature versus time during a typical sulfiding procedure.

Experimental setup for catalytic studies

The experimental system used to carry out this research is shown schematically in Figure 2 and has been described previously.^[20] In short, the setup consisted of an inlet manifold with individual mass flow controllers for regulating the flow of feed gases and an HPLC pump for delivering liquid water that was swept with N₂ through a heated vaporizer, prior to being blended with the rest of the feed. A stainless steel fixed-bed reactor with dimensions of 2.1 cm i.d. and overall length of 39.4 cm was operated isothermally in downward flow mode with temperature control to within $\pm 1^\circ\text{C}$ provided by a fluidized sand bath. Monitoring of the reactor temperature was performed through a series of axially mounted thermocouples located down the side of the reactor (not shown in the schematic). Any air in the system following initial setup was removed by flushing with dry, O₂-free N₂ and the catalyst was maintained under a low N₂ flow (100 mL·min⁻¹) during all overnight and weekend periods. Feeds were brought on- and offline by making use of the system bypass line to ensure the catalyst bed was only exposed to either N₂ or the full challenge stream. During testing, samples of the product stream were taken every 30 minutes for gas chromatography (GC) analysis. The samples were obtained on a dry and sulfur-free basis by pulling the gas stream through a SICAPENT® (P₂O₅) cartridge. For GC analyses, split injections were performed on a Varian 3800 GC with parallel Restek Mol-sieve 5Å and U-Bond columns equipped with thermal conductivity and flame ionized detectors, and a separate Varian CP-3800 GC equipped with an Rt-U-Bond column and pulsed flame photometric and thermal conductivity detectors. N₂ was used as

an internal standard to treat the data, and sulfur and H₂O were calculated based on mass balance. Using CS₂ as an example, conversions were calculated using the following approach:

$$\% \text{Conversion} = 100 \left(1 - \frac{x_{\text{prod.}}(\text{CS}_2)x_{\text{feed}}(\text{N}_2)}{x_{\text{feed}}(\text{CS}_2)x_{\text{prod.}}(\text{N}_2)} \right)$$

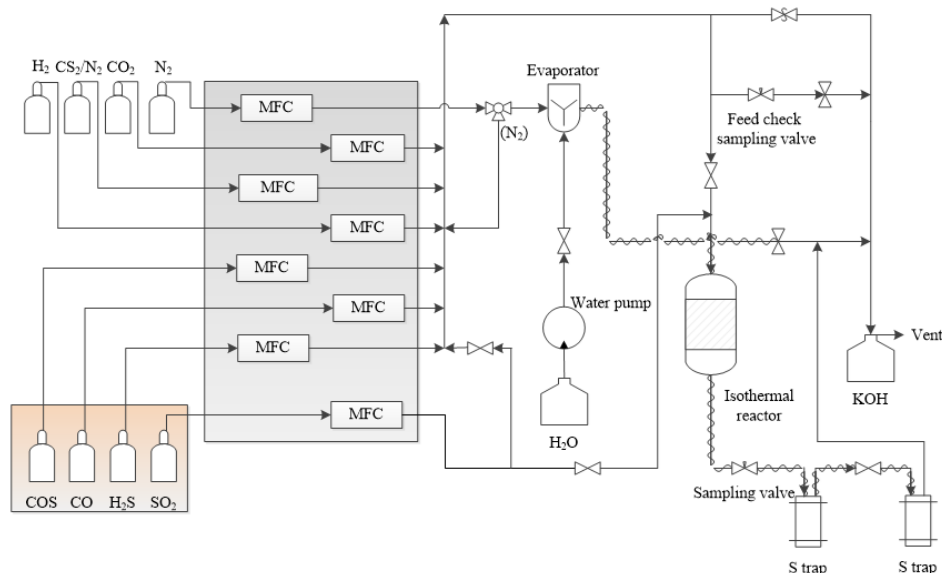


Figure 2. Schematic of experimental setup used for catalyst testing.

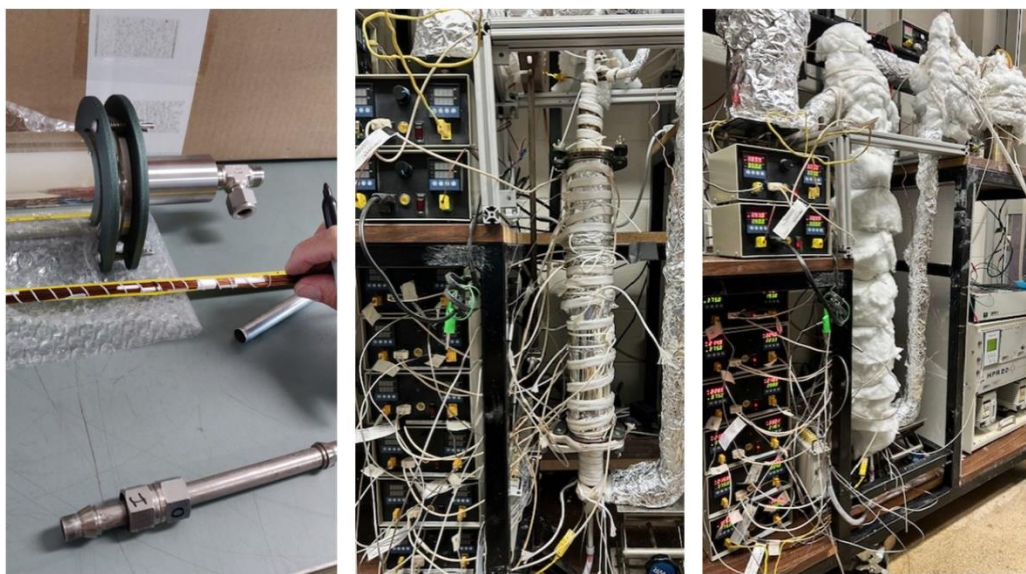


Figure 3. Photographs of the pseudo-adiabatic catalyst testing system showing the base of thermocouple string prior to insertion through bottom flange (left), mirrored and vacuum jacketed glass reactor with top and bottom steel flange attached and heat shields installed (center), and reactor fully insulated and tied into up- and down-stream portions of the system (right).



The reactor used to generate the adiabatic results that will be referenced has also been described in detail previously.^[21] In short, across multiple generations of reactor design and rigorous heat shield calibrations, a novel benchtop scale pseudo-adiabatic reactor was furnished with an internal thermocouple string that allows for 32 temperature measurements within the reactor. This allows for highly resolved in-situ measurement of reaction exotherms across the catalyst bed, providing a wealth of information to be drawn from a single experiment. Improvements are still being made in our reactor design, namely by the incorporation of permanent heat shields, which will help make use of this system more routine. Apart from the reactor, the rest of the experimental setup (*i.e.*, feed inlet manifold and downstream trapping units) are near identical to the isothermal setup described above. See Figure 3 for some relevant photos of the pseudo-adiabatic reactor.

Catalyst testing and conditions

For the isothermal results presented, the base tail gas composition that was used corresponded to 51.101 mol% N₂, 0.617 mol% H₂S, 0.201 mol% SO₂, 0.039 mol% COS, 5.035 mol% CO₂, 0.496 mol% CO, 0.039 mol% CS₂, 2.471 mol% H₂, and balance H₂O. In all cases, the GHSV employed was 1250 h⁻¹ (NTP) and bed temperatures of either 235°C (455°F) or 250°C (482°F) were used. When establishing the baseline for CS₂ conversion across the Al₂O₃ support material with SO₂ present, the SO₂ concentration was raised slightly to provide an H₂S to SO₂ ratio of 2 to 1 for a better comparison to previously established kinetic parameters. When certain components were removed from the feed, the N₂ and / or H₂S flow was adjusted accordingly to maintain the same GHSV.

For the adiabatic results that are referenced, the base tail gas composition that was used corresponded to mol% N₂, 0.604 mol% H₂S, 0.295 mol% SO₂, 0.041 mol% COS, 5.110 mol% CO₂, 0.3 mol% CO, 2.552 mol% H₂, and balance H₂O. In all cases, the GHSV employed was 1250 h⁻¹ (NTP) and a target bed inlet temperature of 250°C (482°F) was used. Similar to the isothermal experiments, when certain components were removed from the feed, the N₂ was adjusted accordingly to maintain the same GHSV.

Safety notes: because this research involved the use of toxic gases H₂S and SO₂, all catalytic tests were conducted in a walk-in bay equipped with high-velocity ventilation, permanent gas detectors, and a caustic scrubbing system. The detectors are interfaced with solenoids controlling air-operated valves to allow (air on) gas flow from a separate and ventilated storage bay. In the case of a leak leading to toxic gas concentrations exceeding 5 ppmv H₂S, 2 ppmv SO₂, or 10 ppmv CO, the air-operated valves close and all toxic gas flow to the experimental system stops.

To avoid confusion for the reader, unless stated otherwise, please assume the experiment being discussed in the next section was performed in the isothermal system.



Results and Discussion

To establish a baseline CS₂ conversion, and to help decipher the role of the deposited CoMo, the tail gas composition was flowed across just the Al₂O₃ support material at isothermal bed temperatures of 235 and 250°C. These temperatures were chosen as they are both within the temperature regime for TGTU hydrogenation reactions. In the absence of CoMo, the Claus equilibrium can be established, and the associated surface sulfate intermediates can accumulate. As mentioned previously, the detrimental effect of surface sulfate on CS₂ conversion is well-established.^[16-18] After a hydrothermal ageing procedure and flowing for *ca.* 40 h, the apparent stabilized CS₂ offered by the Al₂O₃ support, shown in Figure 4, was in excellent agreement with predictions using previously established ASRL kinetic parameters; *ca.* 26% at $T_{bed} = 235^{\circ}\text{C}$ and *ca.* 35% at $T_{bed} = 250^{\circ}\text{C}$.^[15]

In the next sequence of experiments, the tail gas feed was flowed across the fully prepared and sulfided CoMo on Al₂O₃ tail gas catalyst. In one set of experiments, the full tail gas composition was employed, and in the other the SO₂ was removed from the feed and replaced with H₂S to maintain the same GHSV. The corresponding CS₂ conversion product distributions in each of these scenarios is shown in Figure 5. In all cases, CS₂ conversion was quantitative, and the percentages shown in the Figure 5 pie charts represent the selectivity to each of the products. The selectivities for CH₄ and CH₃SH are based on the measured GC results and selectivity to CO₂ was calculated by difference from 100%. Again, we note here the catalyst was made in-house and the reported product distributions may not represent those of a commercial catalyst. However, the trends observed and learnings from the internal comparisons are valid. Interestingly, at both 235 and 250°C, when SO₂ was removed from the feed, a decrease in conversion to CO₂ was observed which was primarily made up for by an increase in conversion to CH₄. A small increase in CH₃SH formation at 235°C was also observed when SO₂ was removed from the feed. Two possible interpretations of these findings include: i) the removal of SO₂ resulted in less competition for hydrogenation active sites, thereby allowing for more CS₂ conversion to proceed via the hydrogenation pathway and / or ii) in the absence of SO₂, reaction 10 cannot proceed, resulting in less conversion to CO₂ which is then made up for by the competitive hydrogenation pathway. More discussion on this and reaction 10 will come later in this paper. However, it is noteworthy that the conversion to CO₂ in all cases here (Figure 5) is higher than what would be expected when considering the hydrolysis rates observed across just the Al₂O₃ support material (Figure 4). Further, with and without SO₂ included in the feed, the lower than expected drop in conversion to CO₂ when the temperature was decreased by 15°C is not in line with our previous studies where the rate of hydrolysis was truly kinetically limited.

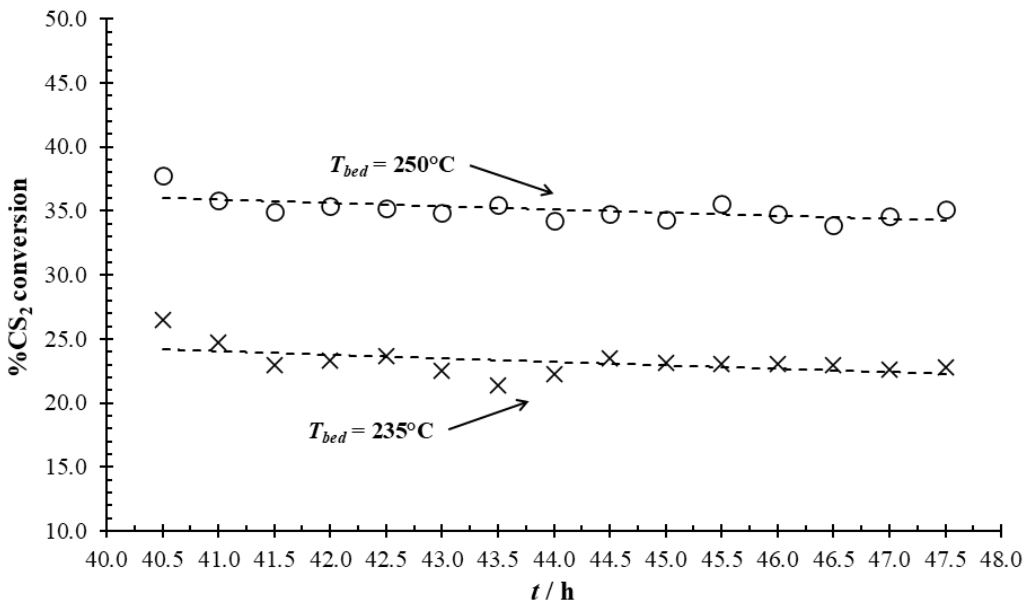


Figure 4. Apparent stabilized CS₂ conversion offered by Al₂O₃ support at isothermal bed temperatures of 235 (x's) and 250°C (hollow circles).

In an effort to identify the true hydrolysis capacity of the CoMo on Al₂O₃ catalyst, a test was performed where the H₂ and CO (source of hydrogen from reaction 5) was removed from the feed. Additionally, SO₂ was removed from the feed to avoid the Claus reaction and any potential direct reaction with CS₂, *i.e.*, reaction 10. The results from a time-on-stream of 30 h probing these conditions are presented in Figure 6. At 250°C, the CS₂ conversion was initially very high, *ca.* 97%, but over the course of two workdays (16 h) was precipitously dropping. When bringing the feed online on the third morning, the catalyst was inadvertently exposed to *ca.* 5% CO for 30 minutes. After realizing, the CO flow was stopped, the correct feed was restored, and the hydrolysis activity was monitored. The temporary exposure to CO, or more likely the H₂ produced from the CO, had the effect of restoring the CS₂ conversion back to its original level of *ca.* 97%. However, like the first two days, in the absence of CO or H₂, the conversion quickly began a precipitous drop-off. This phenomenon was repeated on the fourth day by intentionally introducing 2.5% H₂ back to the feed for a period of 30 minutes. Note the data presented in Figure 6 only correspond to after the temporary CO and H₂ flows were stopped. When the temperature was lowered to 235°C, the CS₂ conversion arguably dropped off even faster. Only trace CH₃SH was observed on the first sample obtained after the exposures to CO and H₂, indicating that the corresponding activity gains were not due to a replenishing of a H₂ reservoir within the catalyst pore structure that temporarily restored the CS₂ hydrogenation pathway. This points towards, under these unique conditions, there was an accumulation of some species on the catalyst surface that inhibited the hydrolysis reaction but was reduced / removed in a facile manner by a temporary exposure to H₂. Pore condensation of elemental sulfur partially fits this theory but H₂S splitting, perhaps facilitated by the molybdenum,^[22] is severely thermodynamically limited in this temperature regime. Alas, a convincing explanation for the drop in CS₂ hydrolysis across the CoMo on Al₂O₃ catalyst with extended time on stream cannot be offered at this time. However, the results indicate that the



capacity for CS₂ hydrolysis on the Al₂O₃ support are much higher than under Claus equilibrium conditions.

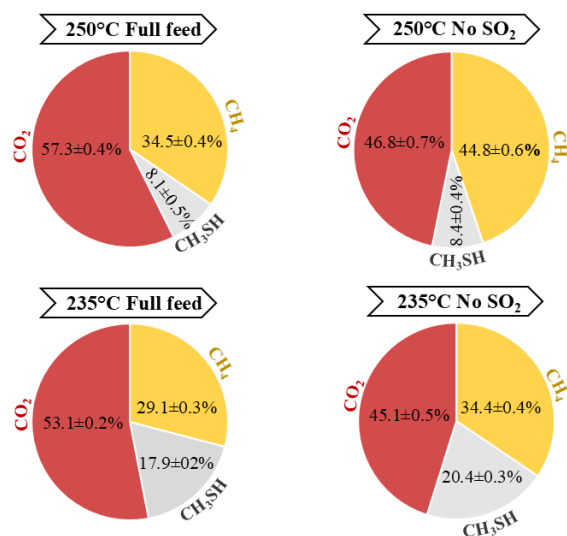


Figure 5. Product distributions offered by the CoMo on Al₂O₃ tail gas catalyst at isothermal bed temperatures of 235 and 250°C, with and without SO₂ as part of the tail gas feed.

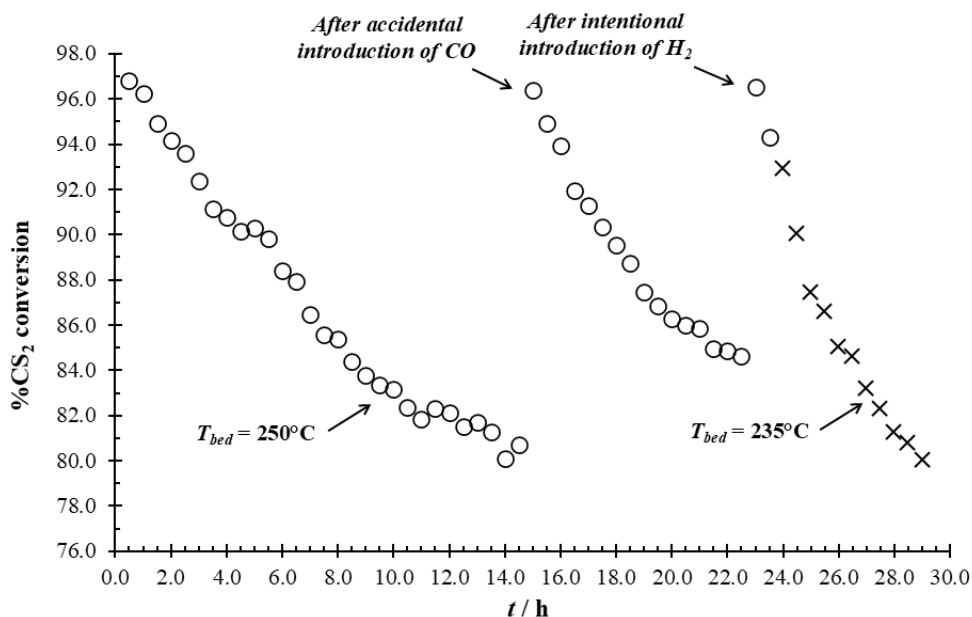


Figure 6. CS₂ conversion data collecting during experiments investigating hydrolysis capacity of CoMo on Al₂O₃ tail gas catalyst at isothermal bed temperatures of 235 (x's) and 250°C (hollow circles).

While using the same feed from directly above (*i.e.*, tail gas composition but with SO₂, CO, and H₂ removed), analogous experiments were performed to investigate the hydrolysis capacity of just



the Al_2O_3 support in the absence of the Claus equilibrium and associated sulfate intermediates. As can be seen in Figure 7, without the deposited CoMo, the Al_2O_3 support offers very stable hydrolysis activity under these conditions and, if anything, increases by several percent over the first 2-3 hours online. Interestingly, the stable level of hydrolysis observed at both temperatures here is in within experimental error of the level observed at the beginning of the analogous experiment with the CoMo on Al_2O_3 catalyst (and where conversion would return to after a temporary exposure to H_2). The hydrothermal ageing procedure had no real impact on hydrolysis activity at 250°C but did afford a slightly lower level of hydrolysis at 235°C .

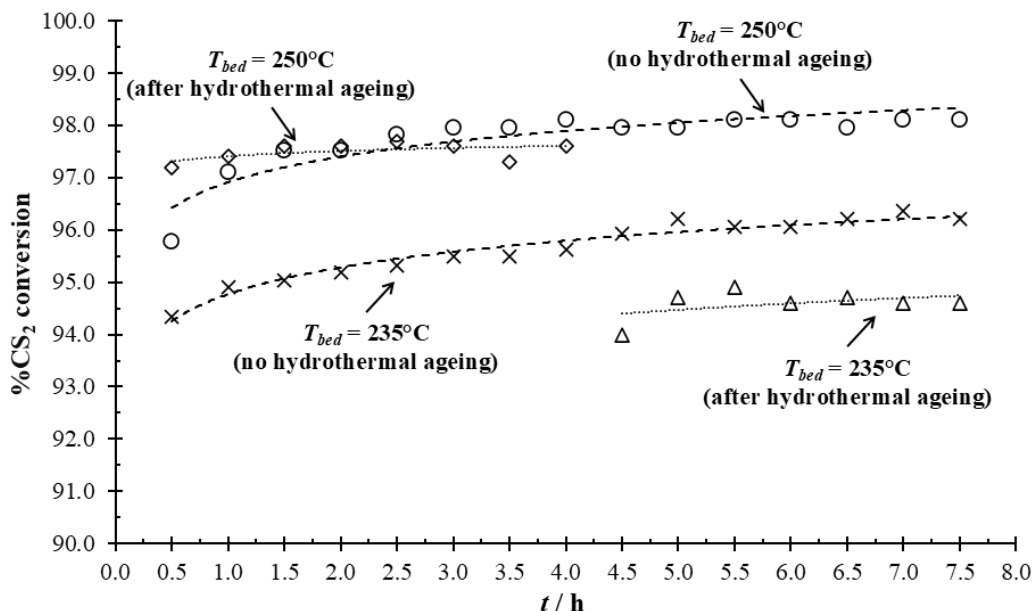


Figure 7. CS_2 conversion data collected during experiments investigating hydrolysis capacity of Al_2O_3 support in the absence of the Claus reaction and its associated intermediates. Hollow diamonds and circles represent data collected at an isothermal bed temperature of 250°C , with and without hydrothermal ageing, respectively. Hollow triangles and x's represent data collected at an isothermal bed temperature of 235°C , with and without hydrothermal ageing, respectively.

In reality, under true tail gas conditions, the hydrolysis capacity of the Al_2O_3 support in the CoMo impregnated catalyst will likely be slightly lower than what is shown in Figure 7. Some of the Al_2O_3 support's surface will undeniably be occupied by the deposited CoMo itself. However, most of the surface area of metal oxide and sulfide materials are made up by small mesopores (typically in the range of 2-5 nm) according to the pore size distributions of these materials.^[23] According to both our laboratory analyses and literature, MoS_2 slabs deposited on Al_2O_3 are larger than 5 nm.^[8,23] As such, they are unlikely to be accommodated within the small pores of the alumina support. This is supported by the CS_2 conversions reported in Figure 7 at 235 and 250°C being in good agreement with initial conversion, and conversions after H_2 exposure, shown in Figure 6.

Furthermore, SO_2 was excluded from the feed used in the experiments above investigating the hydrolysis capacity of the Al_2O_3 support but will indeed be present in an actual tail gas; typically, with a ratio of $> 2:1$ H_2S to SO_2 in a TGTU application. As mentioned above, previous work by



ASRL indicated that at least some SO_2 can take part in the Claus reaction on the Al_2O_3 support of a tail gas catalyst.^[14] The sulfur intermediate was inferred by the detection of car-sul (a low vapour pressure carbon-sulfur containing polymer) on the catalyst after experiments with benzene, toluene, and xylenes (BTX) included as part of the tail gas. Nevertheless, as described, the Claus reaction and its associated intermediates are detrimental to CS_2 hydrolysis. However, based on our recent adiabatic studies, SO_2 react rapidly within the TGTU hydrogenation reactor.^[24] The data presented in Figure 8 shows three different catalyst bed temperature profiles measured in our pseudo-adiabatic reactor: i) the exotherm measured while flowing full Claus tail composition, ii) the exotherm measured while manipulating the feed to maintain the same GHSV but only allowing for SO_2 hydrogenation to take place, and iii) the exotherm measured while manipulating the feed to measure the same GHSV but only allowing for the SO_2 . As can be seen, with a bed inlet temperature of *ca.* 250°C, while the exotherm for the water gas shift reaction only plateaus at $\frac{2}{3}$ of the way into the bed, the hydrogenation of SO_2 appears to be complete in the first $\frac{1}{4}$ of the bed. Of course, CO will occupy some of the same active sites needed for SO_2 hydrogenation and an inlet temperature of 250°C is not feasible with indirect steam reheaters, both of which will have the effect of shifting SO_2 extinction deeper into the bed. However, even before the SO_2 is taken to extinction, the H_2S to SO_2 ratio will be extremely high which, as referenced above, is beneficial for CS_2 hydrolysis (*i.e.*, a higher H_2S to SO_2 ratio leads to lower steady state surface sulfate concentration).

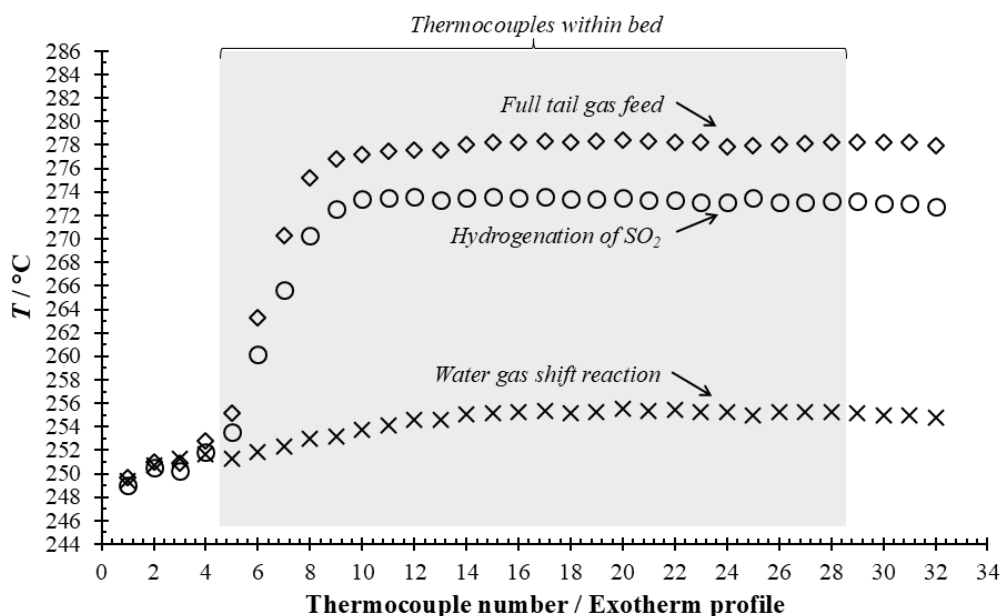


Figure 8. Exotherms measured in the ASRL pseudo-adiabatic reactor when investigating the relative contributions from the water gas shift reaction and the hydrogenation of SO_2 to the overall exotherm when flowing a representative tail gas.

The results collected thus far in the study demonstrate that the reduced surface sulfate under Claus tail gas conditions allow for higher CS_2 hydrolysis rates compared to analogous temperatures under Claus converter conditions. However, for the sake of completeness, a direct reaction between CS_2



and SO_2 (*i.e.*, reaction 10) was still investigated across the Al_2O_3 support and the CoMo on Al_2O_3 catalyst at 235°C (Figure 10). To do this, only N_2 , CS_2 , and SO_2 were used from the tail gas composition and the N_2 flow was adjusted to maintain the same GHSV. Under these conditions, both the Al_2O_3 support material and the CoMo on Al_2O_3 catalyst initially offered high CS_2 conversion, extremely high on the support material alone, but the activity observed in both tests quickly converged and appeared to be trending down with extended time on stream. For the sake of comparison, some similar test results obtained by ASRL in 2001 are also included in Figure 9.^[19] In this previous study by ASRL, the temperature employed was 330°C and, in addition to a lower initial starting point, the conversion also dropped off at a faster rate. All in all, the results suggest that if there is a minor contribution to the overall CS_2 conversion from reaction with SO_2 , the molybdenum is not playing an important role.

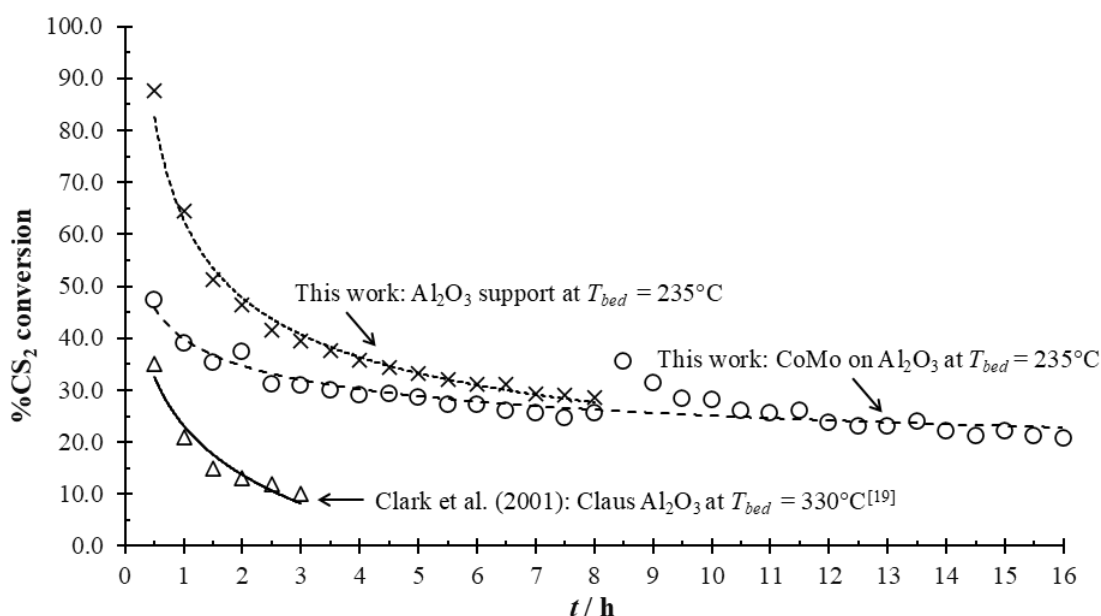


Figure 9. CS_2 conversion data collected during the current ($T_{bed} = 235^\circ\text{C}$) and past studies ($T_{bed} = 330^\circ\text{C}$) investigating a direct reaction between CS_2 and SO_2 (*i.e.*, reaction 1).

A more plausible explanation for the apparent reaction between CS_2 and SO_2 could be related to the mechanism shown in Figure 10. Both fresh and Al_2O_3 that has been exposed to Claus conditions contain surface water in the form of hydroxide groups. The conversions shown in Figure 9 may simply be initiated by residual surface water to generate CS_2 and surface H_2S . Then, as shown in Figure 10, the SO_2 only serves to react with the formed surface H_2S to produce some elemental sulfur and, more importantly, regenerate the surface H_2O so that the cycle can turn over again. Over time, surface H_2O and / or H_2S will undoubtedly be stripped from the surface, and this could explain the decline in CS_2 conversion that is observed in these experiments with extended time on stream. Low ppm levels of H_2S were observed in the effluent in the current study. The higher temperature in ASRL's previous work may be responsible for the sharper drop off in activity.^[19]

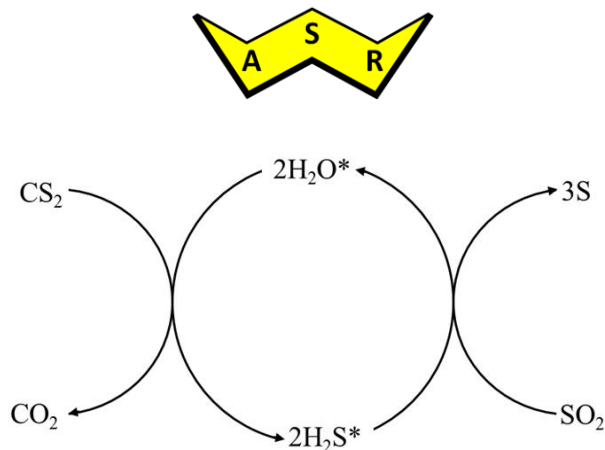


Figure 10. Potential mechanism demonstrating indirect role that SO_2 plays in CS_2 conversion across Claus Al_2O_3 (*indicates surface species).

In support of the above discussion and the impact of Claus intermediates, we have observed Claus Al_2O_3 used in this temperature range to contain *ca.* 1.5-2.0 wt% sulfate.^[25] By contrast, the used CoMo on Al_2O_3 TGTU catalyst examined here yielded a sulfate content of 0.9 wt%. While this value is lower than that observed on Claus alumina, it is nevertheless likely an overestimate of the true in-service sulfate coverage. The catalyst had been stored in air for *ca.* 3 months prior to analysis, allowing for slow oxidation of exposed MoS_2 edge sites. Thus, the measured 0.9 wt% sulfate at best should be interpreted as an upper bound, with the true in-service sulfate fraction expected to be substantially lower. On Claus Al_2O_3 only exposed to H_2S conditions, akin to the last $\frac{3}{4}$ of the TGTU hydrogenation reactor, we have measured sulfate in the 0.2 wt% range.^[25]

Conclusions

The current study revisited the pathways for CS_2 conversion under TGTU-relevant conditions to reconcile the apparent contradiction between established Claus hydrolysis kinetics and the nearly quantitative conversions typically observed across a CoMo on Al_2O_3 hydrogenation catalyst. By systematically comparing the roles of the alumina support, deposited CoMo, and SO_2 , several key insights were obtained:

- Hydrolysis activity of Al_2O_3 is substantially higher under TGTU conditions than under Claus converter conditions, primarily due to the suppression of sulfate accumulation and the rapid extinction of SO_2 within the hydrogenation bed.
- In experiments trying to determine the true hydrolysis capacity of the CoMo on Al_2O_3 catalyst under TGTU conditions, the presence of CoMo complicated interpretation of the results. While initial CS_2 hydrolysis activity was high, it declined with time-on-stream due to the formation of reversible surface species generated by an unknown side reaction. Temporary exposure to H_2 or CO restored activity, indicating that the decline was not due to permanent deactivation. In contrast, the bare Al_2O_3 support exhibited stable hydrolysis under identical conditions, further supporting that the CoMo enables alternative surface chemistry that can interfere with hydrolysis, although such fouling species would not be expected to accumulate under normal TGTU operating conditions.



- The CS₂ hydrogenation pathway competes with hydrolysis, and product distributions indicate that SO₂ influences this competition. Removal of SO₂ decreased CO₂ selectivity (formed from hydrolysis pathway) and increased CH₄ and CH₃SH selectivity (formed from hydrogenation pathway).
- Direct CS₂ + SO₂ reaction was found not to be a significant contributor to overall CS₂ conversion, either across the Al₂O₃ support or the CoMo on Al₂O₃. Any apparent activity can be more plausibly explained by SO₂ turning over a cyclic process involving surface H₂O and H₂S.

Taken together, these findings help rationalize the consistently high CS₂ conversion reported in TGTU operation and reemphasize the sensitivity of CS₂ hydrolysis across Al₂O₃ to Claus reaction intermediates. As such, the nature of TGTU reactor environment allow the inherent hydrolysis activity of alumina to be more effectively exploited, rather than requiring a fundamentally different catalytic pathway. These insights should be valuable for TGTU process modeling, providing more accurate kinetic inputs for CS₂ hydrolysis.



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