

Effects of Sulfur Contamination on Cu-Based Methanol-Synthesis Catalysts: A Structured Review and Quantitative Synthesis

William Park¹

¹North Hollywood High School, Los Angeles, California, USA

Advisor: Grace Kim, iANT Education, graceiantedu@gmail.com

Abstract

Sulfur contamination can deactivate copper-based methanol-synthesis catalysts, but published effects are hard to compare because experiments use different catalysts, exposure methods, and performance measures. This study asked how much sulfur reduces performance and which conditions are linked to greater damage. Each sulfur-exposed result was traced to its source, matched with a clean or pre-exposure value from the same study, and converted to retention and loss. The primary analysis included three studies, nine independent H₂S exposures, and 13 readouts; comparable evidence was unavailable for other sulfur species. Losses ranged from 4.5% to 41.1%. Giving each study equal influence produced a descriptive center of 20.6% loss, not a variance-weighted pooled effect. A random-effects estimate could not be calculated because sample sizes and outcome variances were unavailable and several readouts came from the same exposures. Longer exposure was linked to greater damage in the clearest within-study comparison. Concentration, catalyst formulation, temperature, and exposure method may also matter, but their independent effects could not be separated. The evidence was insufficient for a general sulfur concentration-time predictor. A separate clean-In₂O₃ model was reproduced successfully, but transferred inconsistently and cannot predict sulfur poisoning of Cu/ZnO/Al₂O₃. Overall, H₂S consistently impaired methanol performance, but the effect remained strongly condition-dependent, supporting exposure prevention and standardized reporting.

Keywords: *methanol synthesis; Cu/ZnO/Al₂O₃; sulfur poisoning; hydrogen sulfide; catalyst deactivation; quantitative synthesis; kinetic model transferability*

1. Introduction

Methanol is a major industrial chemical used to make fuels, solvents, plastics, and many other products. It can also be produced by reacting captured carbon dioxide (CO₂) with hydrogen, offering a way to turn captured carbon and renewable hydrogen into a useful liquid product. Copper-based catalysts, especially Cu/ZnO/Al₂O₃, are widely used because they can produce methanol at moderate temperatures and pressures. Their performance, however, depends on the purity of the gas entering the reactor (Zhong et al., 2020; Kattel et al., 2017; Behrens et al., 2012).

Sulfur compounds are a particular concern. Hydrogen sulfide (H₂S), sulfur dioxide (SO₂), carbonyl sulfide (COS), carbon disulfide (CS₂), and sulfur-containing organic compounds can interact with the catalyst surface and lower the number of sites available for methanol synthesis (Wood et al., 1980; Chai et al., 1991; He et al., 2020; Prašnikar & Likozar, 2022; Schühle et al.,

2020; Schittkowski et al., 2018). The damage is not determined by sulfur concentration alone. It may vary with the sulfur species, exposure time, catalyst composition, temperature, pressure, and feed composition. ZnO can act as a sulfur sink and may delay damage to copper, but that protection is limited and depends on the catalyst and exposure conditions (Chai et al., 1991; Schittkowski et al., 2018). Published studies also report performance in different ways, including productivity, yield, selectivity, activity, and rate of decline. Their results therefore cannot be combined directly without careful comparison (Wood et al., 1980; Chai et al., 1991; He et al., 2020; Prašnikar & Likozar, 2022; Schühle et al., 2020).

An earlier phase of this project tested whether published data could support a broader predictive model. It successfully reproduced a published model for clean, unsupported In_2O_3 (Ghosh et al., 2021) and built a traceable system for loading sources, checking experimental conditions, and testing predictions on studies the model had not seen. The workflow worked as intended, but predictions did not transfer reliably between independently prepared catalysts (Becker et al., 2026; Dang et al., 2020; Sun et al., 2015; Sun et al., 2020; Wei et al., 2025; Yang et al., 2020), and the sulfur data were too sparse and inconsistent for a general dose-and-time predictor. The modeling was therefore useful as a diagnostic: it showed that the evidence first had to be screened, matched, and placed on a comparable scale.

This study used a structured literature review and stratified quantitative synthesis to determine how much sulfur contamination reduces the performance of Cu-based methanol-synthesis catalysts across published experiments, and which reported conditions are associated with more severe damage. Wherever possible, each sulfur-exposed result was matched to a clean or pre-exposure result from the same study and expressed as the proportion of performance retained. Direct methanol-production outcomes were analyzed separately from deactivation-rate outcomes. Repeated observations remained grouped by study, while duplicate reports, graph-read values, and experiments without a valid baseline were explicitly identified.

The analysis examined associations with sulfur concentration, exposure time, catalyst formulation, temperature, pressure, feed composition, and exposure protocol. Because these comparisons came from different studies, they were interpreted as associations rather than proof of causation. A general predictor was to be fitted only if the final dataset contained enough independent and comparable evidence. This evidence gate was not met, so the paper emphasizes the quantitative synthesis while retaining the earlier clean- In_2O_3 work as a separate test of model implementation and transferability.

2. Methods

2.1 Study design and literature search

This study uses a structured, source-traced review and stratified quantitative synthesis to examine how sulfur contamination changes the performance of Cu-based methanol-synthesis catalysts. The independent unit of evidence is a physical sulfur-exposure treatment or experimental run. Multiple results from one publication are recorded when relevant, but they remain grouped under the same study; repeated time points or temperatures from one treated sample are not counted as separate experiments (Hedges et al., 2010).

The search began with original papers collected during the earlier impurity-modeling phase and was expanded using targeted combinations of methanol synthesis, copper catalyst terms

such as Cu/ZnO/Al₂O₃ and CuZnAl, and sulfur terms such as H₂S, SO₂, COS, CS₂, thiophene, poisoning, and deactivation. Publisher and DOI records, repositories, supporting-information links, reference lists, forward citations, author searches, theses, reports, and conference records were examined. Reviews were used to locate original experiments but were not counted as experimental evidence. Searching continued until two focused passes found no new directly eligible studies. Because the earlier work did not preserve a complete database-by-database query log, this is described as a structured, source-traced search rather than an exhaustive database review (Campbell et al., 2020).

2.2 Eligibility and study selection

Studies were eligible for the main quantitative synthesis when they reported an original methanol-synthesis experiment using a Cu-based catalyst, direct exposure to a sulfur-containing compound, a numerical methanol-performance outcome, and a defensible clean or pre-exposure comparison from the same study. The catalyst, outcome definition, unit, and major reaction conditions had to be sufficiently similar within each pair. Cu/ZnO/Al₂O₃ formed the main catalyst group; other Cu-based formulations were retained for separate subgroup analysis.

Methanol productivity, formation rate, yield, and clearly defined methanol activity were eligible primary outcomes. Normalized activity was included only when it referred directly to methanol synthesis and had an identifiable baseline. Selectivity-only, conversion-only, surface-characterization, guard-bed, mechanism-only, and methanol-decomposition results did not enter the primary performance synthesis. Deactivation rates and poisoning constants were retained as a separate outcome family.

Records were screened at both the publication and experimental-condition levels. Full papers and supporting information were used when available, while metadata-only records supplied no numerical effects. Related journal articles, theses, reports, conference papers, and mirrored copies were grouped into one publication family, with the clearest primary report supplying the values. The physical exposure or run was treated as the independent unit; repeated observations from one curve or treated sample remained related. Reasons for exclusion or restricted use were recorded.

2.3 Data extraction and quality assessment

Each observation received a Study ID and an Experimental Row ID. The extraction recorded the source and evidence location; catalyst identity and composition; sulfur species, concentration, duration, and exposure method; reaction temperature, pressure, feed, and space velocity; clean and sulfur-exposed outcomes; units; reported uncertainty; extraction method; and study-independence and duplicate groups. Values from tables or text were preferred. Figure-derived values were used only when the axes and comparison were clear and were labeled as digitized or approximate. Missing information was left missing rather than inferred, and nominal and measured sulfur concentrations remained separate.

Evidence was assessed from its source traceability, the validity of the clean comparison, completeness of the exposure protocol, directness of the methanol outcome, comparability of the catalyst and operating conditions, duplicate risk, and uncertainty reporting. These judgments were used for sensitivity analysis, not as statistical precision weights. Scripted checks tested

row identifiers, numeric ranges, baseline availability, outcome compatibility, duplicate status, and study separation.

2.4 Outcome definition

The primary effect was the within-study fraction of performance retained after sulfur exposure:

$$\text{Retention (\%)} = 100 \times (\text{sulfur-exposed performance} / \text{matched clean performance})$$

$$\text{Loss (\%)} = 100 - \text{Retention (\%)}$$

The exposed and clean values had to use the same outcome and unit for the same catalyst under comparable conditions. The preferred reference was the same run before exposure or a matched clean control at a similar time on stream; a baseline from another publication was never substituted. For statistical analysis, the comparison was expressed as the log response ratio, $\ln(\text{sulfur-exposed performance} / \text{matched clean performance})$, where a negative value indicates loss (Hedges et al., 1999). Results were converted back to percentage retention and loss for interpretation. Deactivation-rate outcomes were analyzed separately because a larger rate represents faster damage rather than lower production.

2.5 Analytical choices and rationale

Within-study matching was chosen because absolute catalyst performance and reporting units differed across publications; comparing each sulfur-exposed result with its own clean baseline reduces part of that between-study variation. Retention and loss were reported as percentages because they are unitless and can be interpreted across productivity, yield, formation rate, and normalized activity, while only pairs with the same outcome and unit were matched. The log response ratio was used for calculations because sulfur damage is naturally multiplicative and the log scale treats proportional changes more symmetrically; results were converted back to retention or loss for reporting. Sulfur concentration was converted to ppm only when the conversion was unambiguous, nominal and measured values remained separate, and exposure time remained in hours. Concentration $\times$ time was descriptive rather than a common dose unit because equal products can represent very different poisoning histories. Direct performance outcomes and deactivation rates were kept separate because they answer different questions.

2.6 Quantitative synthesis

Results were separated by outcome and exposure protocol. Continuous cofeed, sulfur pretreatment followed by clean testing, pulsed exposure, slurry operation, and industrial spent-catalyst evidence were not treated as the same process. Direct methanol-output effects were also kept separate from deactivation-rate, proxy, and mechanistic evidence.

Individual effects were reported with their study and protocol, but across-study summaries were study balanced so that papers with many rows did not dominate. When sampling variances were unavailable, the synthesis used individual effects, study-level medians, and ranges; confidence intervals were not created from printed precision or graph resolution. A random-effects meta-analysis was planned only for a comparable outcome–protocol group with

at least three independent studies and usable sample sizes and standard deviations or standard errors. Log response ratios were pooled using restricted maximum likelihood with a small-sample adjustment and then converted back to retention and loss. Studies without adequate variance information remained in the study-balanced synthesis rather than the variance-weighted pool (Hedges et al., 2010; Campbell et al., 2020).

Possible explanations for different effect sizes included sulfur species, concentration, exposure duration and method, catalyst composition, temperature, pressure, feed composition, space velocity, and reactor type. Concentration multiplied by time could be reported as a descriptive exposure index, but concentration and duration remained separate variables. These comparisons were interpreted as associations, not proof that a condition caused greater damage. Sensitivity analyses were performed using directly reported values only, the closest Cu/ZnO/Al₂O₃ catalysts only, H₂S studies only, one exposure protocol at a time, and leave-one-study or publication-family-out checks (Viechtbauer & Cheung, 2010).

2.7 Secondary modeling analyses

The earlier clean-catalyst model was retained as a separate secondary analysis. The published Ghosh et al. single-site Langmuir–Hinshelwood–Hougen–Watson model was coupled to a plug-flow reactor calculation for clean, unsupported cubic In₂O₃ (Ghosh et al., 2021). The unchanged parameter set was labeled M0 and was checked against 32 source-study conditions, then transferred without recalibration to 88 conditions from six other studies (Becker et al., 2026; Dang et al., 2020; Sun et al., 2015; Sun et al., 2020; Wei et al., 2025; Yang et al., 2020). M1 used one fitted multiplier for all reaction rates, whereas M2 used separate multipliers for methanol formation and the reverse water–gas shift reaction. The recalibrations used 55 unique cubic-In₂O₃ conditions from six studies.

Model error was reported as mean absolute error in percentage points because conversion, selectivity, and yield were already percentages, making an error of one point directly interpretable; relative-percent error would overemphasize low-yield conditions. When methanol yield was not reported, it was calculated as conversion × selectivity / 100 and flagged as derived rather than treated as directly reported evidence. Entire studies were held out because a random row split could place conditions from the same catalyst preparation in both training and test sets and overstate transfer (Roberts et al., 2017). Study-balanced summaries gave each publication equal influence, while row-weighted values were retained only as secondary diagnostics.

A separate sulfur-retention model was attempted only if one comparable outcome–protocol group passed a prespecified evidence gate requiring multiple independent studies, adequate concentration and exposure-time coverage, sufficiently complete fields, and enough studies for whole-study holdout testing. The target was log retention, with concentration and duration evaluated separately and only a small number of additional terms. Entire studies, rather than random rows from the same paper, were held out during evaluation. If the evidence gate was not met, no general predictor was fitted and the quantitative synthesis remained the main result.

All transformations and checks were scripted in Python. The final analysis uses one locked, source-traceable table; superseded or quarantined records remain available for audit but do not enter the reported synthesis.

3. Results

3.1 Study selection and usable evidence

The audited source inventory contained 23 records, including original articles, duplicate copies, precursor reports, and excluded studies. After related reports were grouped, eight independent study lineages remained with potentially usable Cu/ZnO/Al₂O₃ and H₂S evidence. Five studies supplied 16 numerical conditions with a clean or pre-exposure methanol comparison. Thirteen directly reported or directly labeled conditions from three studies formed the primary synthesis (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020). These represented nine independent sulfur exposures: six catalyst formulations tested by Chai et al., two pretreatment groups tested by Schühle et al. at three reaction temperatures each, and one continuous-cofeed experiment reported by Prašnikar and Likozar. Repeated temperature measurements from the same poisoned sample were retained as related observations rather than counted as separate exposures. These counts are the author's analysis of the locked source inventory and condition table documented in Supplementary Information Sections S2–S4.

Three additional conditions were kept as secondary evidence. Wood et al. supplied two approximate time-point readings from one continuously exposed catalyst, and Heracleous et al. supplied one retained-yield value calculated from graph-read conversion and selectivity (Wood et al., 1980; Heracleous et al., 2022). He et al. provided a long-duration conversion proxy but no eligible direct methanol outcome (He et al., 2020). All primary quantitative comparisons involved H₂S. The available data therefore did not support a numerical comparison among H₂S, SO₂, COS, CS₂, and organic sulfur compounds.

Table 1. Characteristics of the three studies contributing primary direct H₂S performance data. Readouts from the same physical exposure are not independent. Sources: Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020.

Study	Catalyst	H ₂ S exposure	Exposures / readouts	Methanol outcome	Key limitation
Chai et al. (1991)	Six laboratory CuO/ZnO/Al ₂ O ₃ formulations	Repeated 0.5 h H ₂ S pulses; inlet concentration not reported	6 / 6	Methanol-synthesis activity	Formulations and reactor configuration differed.
Schühle et al. (2020)	Commercial CZA: 63.5% CuO, 24.7% ZnO, 10.1% Al ₂ O ₃ , 1.3% MgO	400 ppm H ₂ S pretreatment for 4 or 18 h	2 / 6	Methanol productivity	Three temperatures are related readouts of each poisoned sample.
Prašnikar & Likozar (2022)	Commercial HiFuel W230 CZA	Continuous 8.1 ppm H ₂ S cofeed for 30 h	1 / 1	Normalized methanol activity	Single experimental concentration; simulated

					long-term curve excluded.
--	--	--	--	--	---------------------------

3.2 Magnitude of the performance loss

The author's analysis of the 13 primary conditions found that sulfur-exposed catalysts retained 58.9–95.5% of their matched clean performance. This corresponds to a loss of 4.5–41.1%. The study-level median retention was 67.7% for Chai et al., 84.2% for Schühle et al., and 90.0% for Prašnikar and Likozar, equivalent to median losses of 32.3%, 15.8%, and 10.0%, respectively (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020). For one equal-study summary, the log response ratios were first averaged within each study and then across the three studies. The resulting descriptive center was 79.4% retention, or a 20.6% reduction in methanol performance. This value is not a variance-weighted pooled estimate. In the leave-one-study-out check, the estimated loss ranged from 14.9% to 25.4%. Figure 1 shows the condition-level effects and study medians. The underlying values and calculations are documented in Supplementary Information Sections S4–S6.

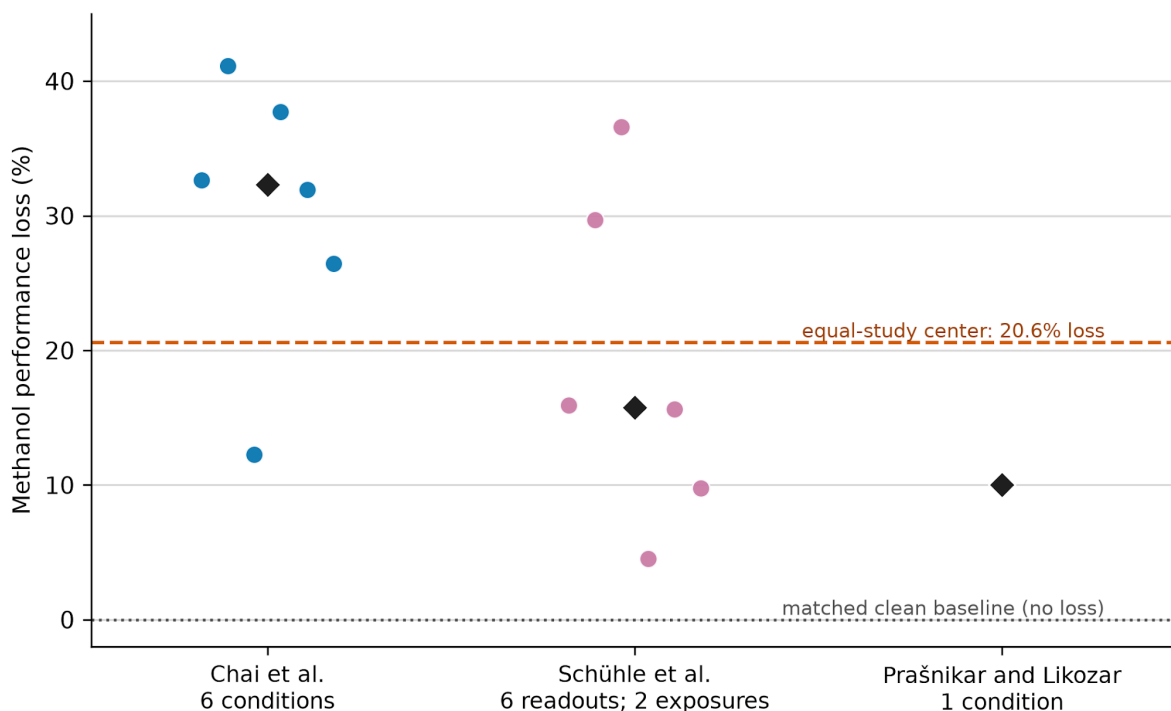


Figure 1. Author's analysis of matched clean-versus-H₂S data from Chai et al. (1991), Prašnikar and Likozar (2022), and Schühle et al. (2020). Each point equals 100 minus the sulfur-exposed/clean performance ratio; higher values indicate greater damage. Black diamonds show study medians, and the dashed line marks the equal-study descriptive center of 20.6% loss. This is not a variance-weighted pooled estimate. The six Schühle readouts come from two poisoned samples and are therefore related.

The spread within studies was also substantial. The six Chai catalyst formulations retained 58.9–87.8% of their original activity after repeated H₂S pulses (Chai et al., 1991). The directly labeled Schühle results ranged from 63.4% to 95.5% retention, depending on pretreatment duration and the temperature used for the later clean-feed performance test (Schühle et al., 2020). In the continuous 8.1 ppm H₂S experiment of Prašnikar and Likozar, normalized activity was 90.0% after 30 h (Prašnikar & Likozar, 2022).

3.3 Conditions associated with greater damage

Exposure duration produced the clearest comparison within a single study. In the Schühle experiment, the author-calculated geometric mean retention across the three reaction-temperature readouts fell from 89.9% after 4 h of 400 ppm H₂S pretreatment to 72.1% after 18 h, an additional 17.8 percentage points of loss (Schühle et al., 2020). The longer treatment caused more damage at every matched readout temperature. After 18 h of exposure, the observed losses were 15.9% at 200 °C, 29.7% at 225 °C, and 36.6% at 250 °C. These temperatures were repeated tests of the same two poisoned samples, however, so they do not establish an independent effect of exposure temperature.

Catalyst formulation was also associated with different losses in the Chai study, where the six formulations showed losses from 12.2% to 41.1% (Chai et al., 1991). Under the same 12-pulse schedule, the Cu-rich formulation retained 62.3% of its clean activity, compared with 73.6% for the Zn-rich formulation. That comparison cannot be converted into a concentration-response relation because the inlet H₂S concentration was not reported, and one high-retention formulation was tested in a different reactor configuration. The result therefore shows formulation-dependent variation within that experiment but does not isolate which composition variable caused it.

The secondary evidence reinforced the importance of concentration, protocol, and time. Across the three continuous-cofeed runs reported by Wood et al., increasing reactor H₂S concentration from 1.3 to 26 $\mu\text{mol L}^{-1}$ increased the activity-decay rate from 0.011 to 0.153 h⁻¹ (Wood et al., 1980). On the 3.2 ppm trajectory, the catalyst retained approximately 50% of its starting activity at 25 h and 25% at 50 h. These time-point values were approximate readings from one longitudinal curve and were not included in the primary summary. For the held-out Heracleous condition, the author-calculated retention from graph-read conversion and selectivity was 81.6% of methanol carbon yield after a 400 ppm, 5 h pretreatment, corresponding to an 18.4% loss (Heracleous et al., 2022). Because the Wood and Heracleous outcomes were derived differently, their contrast with the primary data does not establish a common concentration-response relation. It instead shows why concentration, duration, catalyst, feed, and exposure method could not be separated across studies.

3.4 Statistical synthesis and sulfur-model feasibility

None of the three primary studies reported the sample sizes and outcome variances needed for an inverse-variance meta-analysis of the matched retention effects. No outcome-protocol group contained at least three independent studies with usable uncertainty data. A random-effects pooled estimate, confidence interval, and heterogeneity statistic were therefore not calculated. The reported synthesis consists of individual effects, study-level medians and ranges, and the equal-study descriptive summary above. The absence of required pooling

inputs was confirmed in the three source studies (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020), and the descriptive approach follows dependence-aware and synthesis-without-meta-analysis principles (Hedges et al., 2010; Campbell et al., 2020).

The prespecified modeling gate was also not met. Only three independent primary exposures had both a reported H_2S concentration and duration: two pretreatments from Schühle et al. and one continuous-cofeed experiment from Prašnikar and Likozar (Prašnikar & Likozar, 2022; Schühle et al., 2020). Combining them would make concentration inseparable from study and protocol, while the Chai data could not fill the gap because inlet concentration was missing (Chai et al., 1991). No final general predictor was therefore fitted to the locked meta-analysis dataset. The earlier modeling work still contributed a reproducible source-tracing, harmonization, and study-held-out testing workflow, but the final evidence supported protocol-bounded descriptions rather than a transferable concentration-time model.

3.5 Secondary clean- In_2O_3 model reproduction and transfer

The earlier clean-catalyst modeling was retained as a separate secondary analysis because it addressed a different catalyst and question. The published Ghosh et al. model for clean, unsupported cubic In_2O_3 contains no sulfur term and does not describe $\text{Cu/ZnO/Al}_2\text{O}_3$ poisoning (Ghosh et al., 2021). With the published parameters unchanged (M0), the implementation reproduced 32 source-study conditions; external transfer was then tested on 88 clean-feed conditions from six independent studies (Becker et al., 2026; Dang et al., 2020; Sun et al., 2015; Sun et al., 2020; Wei et al., 2025; Yang et al., 2020).

In the stricter 55-condition cubic subset, whole-study-held-out methanol-yield MAE was 1.729 percentage points for M0, 1.789 for M1, and 1.958 for M2 (Roberts et al., 2017). Each recalibrated model improved held-out yield in only three of six studies, so M0 was retained. The implementation and testing therefore succeeded, but recalibration did not improve transfer consistently. This secondary result is not evidence about sulfur poisoning. Full equations, assumptions, external-transfer results, and diagnostics are reported in the Supplementary Information Sections S7–S10, Table S7, and Figure S1.

4. Discussion

4.1 Overall interpretation

This study provides a clear but bounded answer to the research question. H_2S reduced methanol-synthesis performance in every eligible primary comparison. Across 13 matched readouts representing nine independent exposures from three studies, the observed losses ranged from 4.5% to 41.1% (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020). Giving each study equal influence produced a descriptive center of 20.6% loss. This value is useful for summarizing the available evidence, but it is not a universal poisoning factor or the expected loss for a commercial catalyst. The broad range is equally important: sulfur damage was consistent in direction, while its magnitude depended strongly on the experiment.

Exposure duration produced the clearest within-study pattern. In the Schühle experiment, extending a 400 ppm H_2S pretreatment from 4 to 18 h reduced geometric mean performance retention from 89.9% to 72.1%, and the longer exposure caused greater loss at every later test temperature (Schühle et al., 2020). This supports duration as a modifier under that protocol, but

it does not establish a general time-response equation. Catalyst formulation was also associated with different outcomes in the Chai experiment, where losses across six formulations ranged from 12.2% to 41.1% under a shared pulse schedule (Chai et al., 1991). Because several composition variables differed together and inlet H_2S concentration was not reported, the results demonstrate formulation-dependent tolerance without proving that one component, such as zinc, independently caused the difference.

The secondary evidence suggests that concentration and continuing exposure may also affect the rate and extent of deactivation. Wood et al. reported faster activity decline at higher H_2S concentrations and progressive loss along a continued-exposure trajectory (Wood et al., 1980). Those measurements, however, were deactivation rates and approximate time points rather than the direct methanol outcomes used in the primary synthesis. Differences in catalyst composition, reactor design, feed, baseline, and exposure method also prevent direct ranking across studies (Wood et al., 1980; Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020; Heracleous et al., 2022). The literature therefore identifies plausible modifiers—especially duration, concentration, formulation, and protocol—but cannot determine how much each contributes independently.

4.2 Evidence strength and limitations

The analysis was strengthened by comparing each sulfur-exposed result with a clean or pre-exposure baseline from the same study. Expressing outcomes as percentage retention allowed differently reported methanol measures to be interpreted on a common scale while reducing the influence of differences in absolute activity. Grouping related observations by study and using an equal-study descriptive center also prevented papers with more reported rows from dominating the summary. These choices improved comparability, but they could not remove the underlying differences among experiments (Hedges et al., 1999; Hedges et al., 2010; Campbell et al., 2020).

A conventional inverse-variance pooled estimate was not justified. The three primary studies did not report the combination of sample sizes and outcome variances needed for statistical weighting, confidence intervals, or a reliable heterogeneity estimate (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020; Hedges et al., 2010; Campbell et al., 2020). Some observations were also related; for example, the six Schühle readouts came from only two poisoned samples tested at several temperatures (Schühle et al., 2020). Treating them as independent would overstate the amount of evidence. In addition, every primary quantitative comparison involved H_2S . The observed range and descriptive center should therefore not be generalized to SO_2 , COS , CS_2 , or sulfur-containing organic compounds. The strongest supported conclusion is that H_2S damage was consistent and often substantial, but its precise severity remained condition-dependent.

4.3 Contribution of the modeling work

The modeling work supports this interpretation without becoming the paper's central claim. The published model for clean, unsupported In_2O_3 was reproduced successfully, confirming that the equations and implementation functioned as intended (Ghosh et al., 2021). Testing on independent clean-catalyst studies then showed that recalibrated versions did not improve methanol-yield prediction consistently when entire studies were held out (Becker et al., 2026;

Dang et al., 2020; Sun et al., 2015; Sun et al., 2020; Wei et al., 2025; Yang et al., 2020; Roberts et al., 2017). These results concern a different catalyst, contain no sulfur term, and cannot predict poisoning of Cu/ZnO/Al₂O₃. A separate sulfur predictor was also not fitted because only three independent primary exposures reported both H₂S concentration and duration, making those variables inseparable from study and protocol (Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020). The modeling outcome is therefore methodological rather than predictive: reproduction within a source study did not guarantee transfer to new studies, and the sulfur literature was not yet sufficiently standardized for a defensible general model.

4.4 Implications

For catalyst operation, the findings support minimizing sulfur exposure and considering exposure duration alongside concentration. Exposure method, catalyst formulation, and operating conditions should also be considered. However, the present evidence does not define a universally safe H₂S threshold or establish that one formulation will always be more resistant. Catalyst-specific testing under the intended feed and reactor conditions remains necessary (Wood et al., 1980; Chai et al., 1991; Prašnikar & Likozar, 2022; Schühle et al., 2020; Schittkowski et al., 2018).

Future studies could make a stronger pooled analysis and transferable model possible by reporting measured sulfur concentration, exposure duration and method, catalyst composition, reactor conditions, matched clean-aging baselines, direct methanol outcomes, replicate counts, and uncertainty. Measurements after sulfur removal would also help distinguish reversible inhibition from lasting deactivation. With more independent studies and consistent reporting, future analyses could estimate uncertainty, compare sulfur species, and separate the effects of concentration and time.

5. Conclusion

This quantitative synthesis shows that sulfur contamination consistently reduces the performance of Cu-based methanol-synthesis catalysts, although the magnitude of damage varies markedly across experimental conditions. Across the primary matched comparisons, the equal-study descriptive center was a 20.6% loss in methanol performance. This value summarizes the available evidence; it is not a variance-weighted pooled effect or a universal prediction for every catalyst and operating condition. Longer exposure was associated with greater deterioration in the clearest time-resolved experiment, while sulfur level, catalyst formulation, temperature, and exposure protocol also appeared to influence severity. However, differences in study design and reporting prevented their independent effects from being quantified reliably.

The main conclusion is therefore both practical and methodological: even limited sulfur exposure can meaningfully impair methanol synthesis, but the literature cannot yet support a broadly applicable dose–response relationship. The secondary modeling work reached the same boundary, succeeding technically but lacking sufficiently standardized sulfur data for reliable generalization. Future experiments should report matched clean controls, sulfur concentration and duration, catalyst composition, direct methanol outcomes, uncertainty, and recovery behavior. More consistent reporting would allow future meta-analyses to move from descriptive synthesis toward robust prediction.

Data and Code Availability

The processed extraction tables, analysis scripts, tests, and generated results are maintained in the author's project repository. The reproducibility package records exact dependencies, file hashes, the source-to-output map, and a release-safety audit. A public release with an archived DOI is planned; copyrighted article PDFs will not be distributed. Supplementary Information Section S11 documents the reproduction commands and authoritative paths.

References

- [1] Becker M, et al. Dopant-controlled oxygen vacancy dynamics define CO₂-to-methanol catalysis on In₂O₃. *Nat Commun.* 2026;17:6435. <https://doi.org/10.1038/s41467-026-72876-w>
- [2] Behrens M, et al. The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science.* 2012;336:893–897. <https://doi.org/10.1126/science.1219831>
- [3] Campbell M, et al. Synthesis without meta-analysis (SWIM) in systematic reviews: reporting guideline. *BMJ.* 2020;368:l6890. <https://doi.org/10.1136/bmj.l6890>
- [4] Chai G, Ai D, Li C. Sulfur poisoning and tolerance of methanol synthesis catalysts. *Stud Surf Sci Catal.* 1991;68:539–547. [https://doi.org/10.1016/S0167-2991\(08\)62681-6](https://doi.org/10.1016/S0167-2991(08)62681-6)
- [5] Dang S, et al. Rationally designed indium oxide catalysts for CO₂ hydrogenation to methanol with high activity and selectivity. *Sci Adv.* 2020;6:eaaz2060. <https://doi.org/10.1126/sciadv.aaz2060>
- [6] Ghosh S, Sebastian J, Olsson L, Creaser D. Experimental and kinetic modeling studies of methanol synthesis from CO₂ hydrogenation using In₂O₃ catalyst. *Chem Eng J.* 2021;416:129120. <https://doi.org/10.1016/j.cej.2021.129120>
- [7] He J, et al. Influence of contaminants in steel mill exhaust gases on Cu/ZnO/Al₂O₃ catalysts applied in methanol synthesis. *Chem Ing Tech.* 2020;92(10):1525–1532. <https://doi.org/10.1002/cite.202000045>
- [8] Hedges LV, Gurevitch J, Curtis PS. The meta-analysis of response ratios in experimental ecology. *Ecology.* 1999;80:1150–1156. [https://doi.org/10.1890/0012-9658\(1999\)080\[1150:TMAORR\]2.0.CO;2](https://doi.org/10.1890/0012-9658(1999)080[1150:TMAORR]2.0.CO;2)
- [9] Hedges LV, Tipton E, Johnson MC. Robust variance estimation in meta-regression with dependent effect size estimates. *Res Synth Methods.* 2010;1:39–65. <https://doi.org/10.1002/jrsm.5>
- [10] Heracleous E, et al. Valorization of steel-work off-gases: Influence of impurities on the performance of Cu-based methanol synthesis catalyst. *Chem Eng J.* 2022;444:136571. <https://doi.org/10.1016/j.cej.2022.136571>

- [11] Kattel S, et al. Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts. *Science*. 2017;355:1296–1299. <https://doi.org/10.1126/science.aal3573>
- [12] Prašnikar A, Likozar B. Sulphur poisoning, water vapour and nitrogen dilution effects on copper-based catalyst dynamics, stability and deactivation during CO₂ reduction reactions to methanol. *React Chem Eng*. 2022;7(5):1073–1082. <https://doi.org/10.1039/D1RE00486G>
- [13] Roberts DR, et al. Cross-validation strategies for data with temporal, spatial, hierarchical, or phylogenetic structure. *Ecography*. 2017;40:913–929. <https://doi.org/10.1111/ecog.02881>
- [14] Schittkowski J, et al. Methanol synthesis from steel mill exhaust gases: challenges for the industrial Cu/ZnO/Al₂O₃ catalyst. *Chem Ing Tech*. 2018;90:1419–1429. <https://doi.org/10.1002/cite.201800017>
- [15] Schühle P, Schmidt M, Schill L, Riisager A, Wasserscheid P, Albert J. Influence of gas impurities on the hydrogenation of CO₂ to methanol using indium-based catalysts. *Catal Sci Technol*. 2020;10(21):7309–7322. <https://doi.org/10.1039/D0CY00946F>
- [16] Sun K, et al. A highly active Pt/In₂O₃ catalyst for CO₂ hydrogenation to methanol with enhanced stability. *Green Chem*. 2020;22(15):5059–5066. <https://doi.org/10.1039/D0GC01597K>
- [17] Sun K, et al. Hydrogenation of CO₂ to methanol over In₂O₃ catalyst. *J CO₂ Util*. 2015;12:1–6. <https://doi.org/10.1016/j.jcou.2015.09.002>
- [18] Viechtbauer W, Cheung MWL. Outlier and influence diagnostics for meta-analysis. *Res Synth Methods*. 2010;1:112–125. <https://doi.org/10.1002/jrsm.11>
- [19] Wei Z, et al. An experimental and computational investigation on structural evolution of the In₂O₃ catalyst during the induction period of CO₂ hydrogenation. *Chin J Catal*. 2025;72:301–313. [https://doi.org/10.1016/S1872-2067\(25\)64657-2](https://doi.org/10.1016/S1872-2067(25)64657-2)
- [20] Wood BJ, Isakson WE, Wise H. Kinetic studies of catalyst poisoning during methanol synthesis at high pressures. *Ind Eng Chem Prod Res Dev*. 1980;19(2):197–204. <https://doi.org/10.1021/i360074a013>
- [21] Yang B, et al. Comparative study of CO₂ hydrogenation to methanol on cubic bixbyite-type and rhombohedral corundum-type indium oxide. *Chin Chem Lett*. 2020;31(10):2627–2633. <https://doi.org/10.1016/j.cclet.2020.05.031>
- [22] Zhong J, et al. State of the art and perspectives in heterogeneous catalysis of CO₂ hydrogenation to methanol. *Chem Soc Rev*. 2020;49:1385–1413. <https://doi.org/10.1039/C9CS00614A>