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H_2S-driven sensitization and inhibition of CH_4 oxidation: An experimental and wide-range kinetic-modeling study

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ABSTRACT

The recent diversification of the energy sources has brought about a renewed interest in hydrogen sulfide (H_2S) chemistry and its mutual interaction with conventional fuels. In this work, the oxidation of methane (CH_4) with and without the addition of 500 ppm H_2S was experimentally investigated in a jet-stirred reactor, at near-atmospheric conditions (107 kPa), low temperatures (450 to 1200 K) and lean-to-rich compositions ($0.5 \leq \Phi \leq 2$), with a residence time $\tau = 2$ s. At the same time, a kinetic model was set up to shed light on the fundamental couplings between carbon and sulfur chemistry.

For all the conditions, the presence of H_2S caused an earlier oxidation onset of CH_4 consumption, compared to the pure fuel. On the other hand, H_2S consumption occurred over a wider temperature range, starting at temperatures as low as 650 K. The kinetic model was able to unravel the interactions resulting in this behavior: the two fuels were found to interact at both radical pool level (OH/O/H), as well as at fuel radical level, through mutual H-abstraction ($CH_3+H_2S \leftrightarrow CH_4+SH$) and radical recombination providing methanethiol ($CH_3+SH \leftrightarrow CH_3SH$). While fuel–fuel H-abstraction was found to significantly affect only the low-temperature behavior, the importance of CH_3SH chemistry was framed in a wider range of conditions. The extended model validation confirmed indeed an inhibiting effect of CH_3SH in the higher-temperature flame propagation of dual-fuel mixtures, whose flame speed had been previously observed to be lower than those of pure fuels.

1. Introduction

The progressive integration of unconventional fuels in the energy market is resulting in new scientific and technological challenges to be overcome, in order to ensure their efficient and harmless exploitation. They also include shale gas [1], and within the undergoing energy transition, biogas, and biooils produced from the fast pyrolysis of lignocellulosic biomass [2]. In all of them, trace amounts of sulfur compounds are present, from tens to thousands of parts per million (ppm), needing proper treatment ahead of fuel utilization.

The Claus process [3] is currently the leading technology used for removing H_2S by converting it into elemental sulfur. Although enhancements such as oxygen-enriched air streams have been introduced to enhance sulfur recovery and process variable H_2S concentrations [4], the direct combustion of untreated gas has been recently proposed as a cost-effective alternative, with a downstream removal of Sulfur Oxides (SO_x) [5,6].

Exploring such a technological pathway requires a thorough knowledge of the combustion chemistry of sulfur-containing compounds, which are mostly present under the form of Hydrogen Sulfide (H_2S) [2]. Indeed, although the lack of understanding in H_2S oxidation chemistry has been partially filled in the latest years, tackling such a topic also includes unraveling the effect of H_2S on the oxidation features of other hydrocarbons. As a matter of fact, the recent literature has shown that even small amounts of H_2S are able to alter the reactivity of hydrogen [7], syngas [8] and methane [9–14]. Such mixtures have actually shown a complex, non-linear behavior, exhibiting effects in the opposite directions: when doping H_2/O_2 mixtures with H_2S, Mathieu et al. [7] showed an increase in the Ignition Delay Time (IDT) of H_2, except at high pressures (33 atm) and low temperatures (< 1100 K), with higher amounts of H_2S (1600 ppm). A comparable behavior was later observed when adding H_2S impurities to syngas (H_2/CO) blends [8].

Moving to CH_4/H_2S co-oxidation, Gersen et al. [11] showed that, at pressures between 30 and 80 bar, the addition of 1% H_2S resulted in halving the IDTs of pure CH_4. Still at high pressures (50 bar), when studying the oxidation of binary mixtures in a Flow Reactor (FR), they showed that H_2S consumption begins much before the onset of CH_4

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oxidation (i.e. even before 600 K). Such effect was similarly observed by Colom-Díaz et al. [12] in FR conditions, for a wide range of pressures (0.65–40 bar) and equivalence ratios. In particular, the oxidation onset of CH_4 was found to occur at lower temperatures compared to the pure fuel (especially at high pressures), while H_2S oxidation was delayed by the presence of CH_4 at atmospheric conditions. Finally, Laminar Flame Speed (LFS) experiments [14–16] showed that replacing CH_4 with H_2S resulted in a decrease of LFS values in stoichiometric and rich conditions.

At a theoretical level, few works investigating the interaction between H_2S and CH_4 were carried out in the last decade. They were mostly focused on the evaluation of H-abstractions by the SH radical from hydrocarbons [17] as well as by S/SO/S_2 [18]. As a result, even the most recent kinetic models had to include several estimations and/or rate rules, like those proposed by Van de Vijver et al. [19] for alkyl sulfide pyrolysis, later implemented in further works [14,20]. When setting up a detailed mechanism for the oxy-combustion of sour gas, Bongartz and Ghoniem [21] pointed out that even a data-driven optimization procedure was not enough to ensure a satisfactory agreement in all the literature datasets (e.g. FR, LFS). The successive kinetic modeling works were mostly performed in support of the respective experimental campaigns [11–14], and highlighted the challenges in obtain a kinetic mechanism with a sufficient degree of generality.

The mentioned experimental works highlight that the most critical region is represented by low-temperature operating conditions, where fuel–fuel interactions might play an important role in regulating the radical pool due to the slower reactivity. In this context, this work aims at framing the role of such interactions through a combined experimental and modeling approach: a novel campaign was performed in a Jet Stirred Reactor (JSR) under diluted conditions, and with variable equivalence ratios (lean to rich). To the authors' knowledge, this is the first time CH_4/H_2S co-oxidation was studied in a JSR facility. A comprehensive analysis of reactants, products and intermediates was carried out. At the same time, by building upon a core H_2S mechanism previously set up, a kinetic mechanism describing CH_4/H_2S oxidation was developed. This was leveraged to gain a more comprehensive understanding of the results from the experimental device, identifying the key steps and competitions driving reactivity, and to obtain indications about future theoretical and kinetic-modeling research.

2. Methodology

2.1. Experimental setup

The oxidation of methane doped with hydrogen sulfide was experimentally investigated using a jet-stirred reactor (JSR) already described in previous works [22,23], working close to atmospheric pressure (107 kPa), and operated at steady state. The reactor consists of a spherical vessel with injection of the fresh mixture through four nozzles located at its center, creating high turbulence resulting in homogeneity in composition and temperature. As a result, the JSR can be modeled as a perfectly stirred reactor. Experiments were carried out at temperatures ranging from 450 to 1200 K and at a residence time τ = 2.0 s. The mixtures composition is reported in Table 1. Six fuel blends were considered, with and without H_2S to assess its chemical role. All the fuel mixtures were composed of 2% CH_4 and 500 ppm H_2S (where present), with helium as dilution gas. Three equivalence ratios (Φ) were considered (0.5, 1.0 and 2.0). The fuel-air equivalence ratio was calculated according to the two following stoichiometric equations: $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$, and $H_2S + 1.5O_2 \rightarrow H_2O + SO_2$. Mass flow controllers were used for reactor feeding (relative uncertainty of ±0.5% in flow). Gases were provided by Messer (H_2S at 925 ±2 ppm in helium, purities of 99.99% for helium and oxygen) and Air Liquide (CH_4 99.995% pure).

The fused silica wall of the JSR was treated with a solution of boric acid (boric acid in 50% water - 50% ethanol) to form an impervious layer of boric oxide to avoid undesirable catalytic effects that were observed in the present study. The occurrence of wall catalytic effects had already been observed in a previous work on H_2S [24] and was also reported by others [25]. The following methodology, inspired by the literature [25], was followed to treat the wall: the tube was first filled with a saturated solution of boric acid, then it was drained and dried with helium flowing through. The tube was heated to 393 K to eliminate the remaining solvent molecules. To obtain the impervious layer covering the wall, the reactor was then time heated at 500 °C (773 K): the obtained layer was white and translucent before the heating, and became invisible after the heating, as mentioned in literature. The procedure was repeated twice as the geometry of the fused silica jet-stirred reactor is complex. Although the washing of the boric oxide layer over time cannot be excluded, no deviations in data were observed during the time of these experiments (more than one month), thus suggesting longer time scales for washing to eventually occur.

Table 1
Experimental conditions (He as balance gas).

Exp ID	CH_4 [–]	H_2S [ppm]	O_2 [–]	Φ [–]
1	0.02	–	0.08	0.5
2	0.02	–	0.04	1
3	0.02	–	0.02	2
4	0.02	500	0.0815	0.5
5	0.02	500	0.04075	1
6	0.02	500	0.0204	2

The reactants and reaction products were analyzed using two diagnostics, gas chromatography and on-line mass spectrometry: (1) a first gas chromatograph (GC) was used for the quantification of carbon-containing species such as methane, carbon monoxide, carbon dioxide and the three C_2 hydrocarbons (the carrier gas was helium). It was equipped with a PlotQ capillary column and included a Flame Ionization Detector (FID) preceded by a methanizer (for the reduction of oxygenated functional groups over a heated nickel catalyst) allowing a better sensitivity for CO and CO_2. (2) a second gas chromatograph was used for the detection of O_2. It was equipped with a Carbosphere packed column and a thermal conductivity detector. Calibrations of both gas chromatographs were performed using gaseous standards or using the "effective carbon number" method for carbon containing species [23]. Relative uncertainties in mole fractions of species detected by gas chromatography are ±5% for methane, O_2, CO and CO_2 and ±10% for C_2 hydrocarbons. (3) On-line mass-spectrometry was used to detect hydrogen sulfide, sulfur dioxide, water, and hydrogen. Sampling was achieved through a capillary tube directly connecting the JSR outlet and the analyzer. This technique requires the calibration of each species as there is no obvious relationship between their structures and their calibration factors. Gaseous standards were used except for water, which was calibrated considering the reaction complete at the highest temperature. It is ±10% for calibrated species (H_2S, SO_2, and H_2) and ±20% for water. Atom-balances were performed for C, H and S. Overall C and H balances are correct over the whole temperature range and whatever the equivalence ratio (1.02 ± 0.06 and 0.99 ± 0.04 for C and H in the mixture case, 1.02 ± 0.05 for C in the neat methane case, respectively). The S balance is also acceptable (overall 1.00 ± 0.06) with slightly more deviations under lean conditions than under stoichiometric and rich ones.

It is worth mentioning that, due to its potential importance in the experimental conditions investigated, a search for CH_3SH was also performed, but it could not be observed in gas chromatography analyses, nor in mass spectrometry ones. This might be due to the loss of this species at the wall of the pipes used for transferring species from the reactor to the analytical section.

2.2. Kinetic modeling

The kinetic modeling of the pyrolysis and oxidation of CH_4/H_2S mixtures was performed through a hierarchical approach. With regard

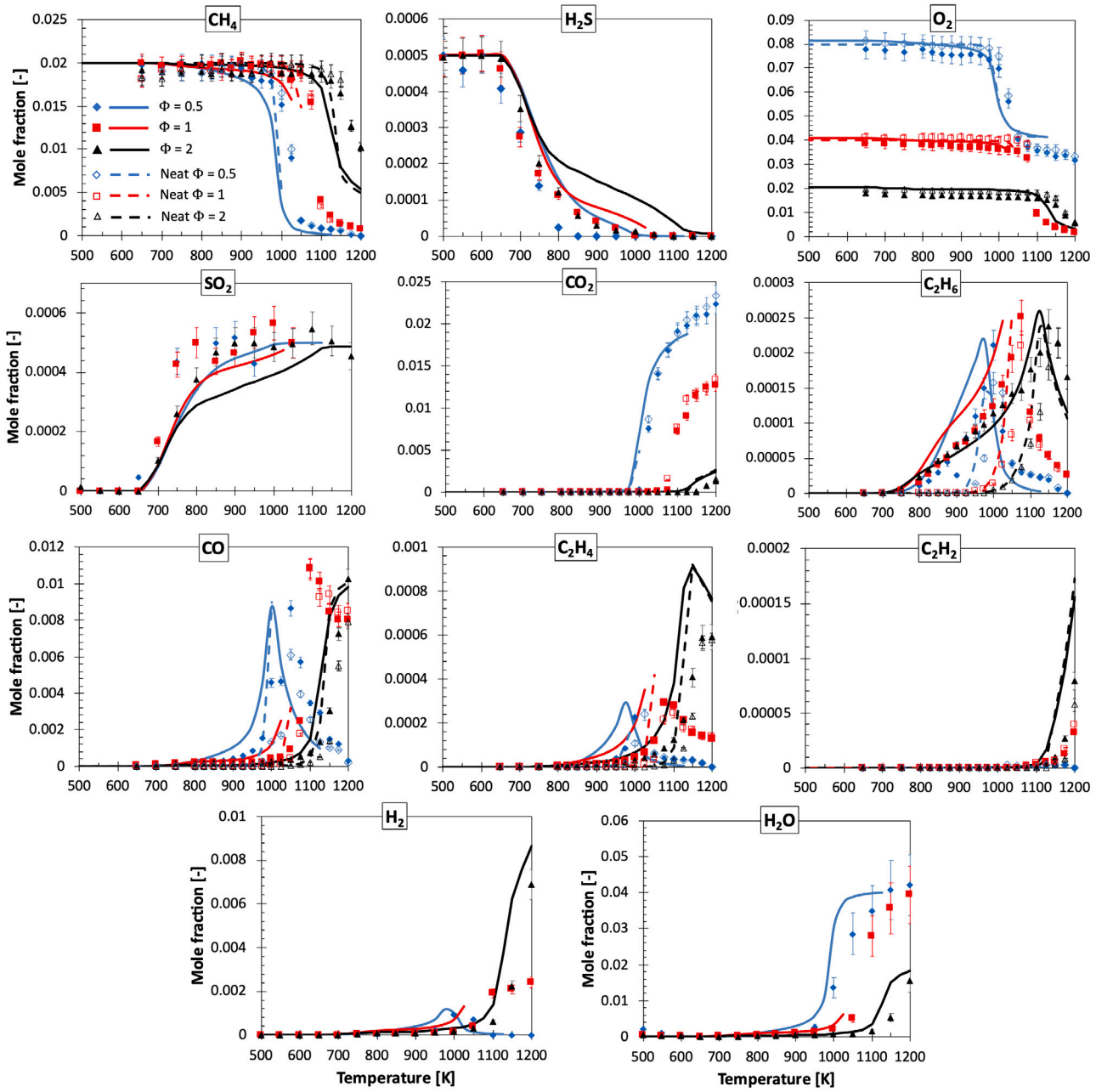

Fig. 1. Mole fractions of reactants, main reaction products and intermediates at variable T and Φ in the JSR. Symbols: experiments. Lines: data computed with the kinetic model when the steady state regime was established.

to CH_4, this was set up with a core C_0-C_2 module from Metcalfe et al. [26], and C_3 from Burke et al. [27]. Such a core mechanism is common to the whole CRECK kinetic framework, and was shown to provide reasonably good predictions for a variety of fuels, against a wide range of experimental conditions and datasets [28]. On the other hand, H_2S sub-mechanism relied on the previous work by Stagni et al. [24] for the pure fuel, where several key reaction steps were re-evaluated through a first-principles methodology, based on an *ab initio*, transition state theory based master equation (ME) approach [29]. With regard to the C-S interactions, they were organized with a modular methodology:

i The H-abstraction by CH_3 from H_2S was taken from the database of H-abstractions evaluated *ab initio* in the recent work of Cavallotti et al. [29]. On the other hand, H-abstractions by SH from heavier hydrocarbons, and by S/SO/S_2 from methane were taken from the works of Zeng et al. [17,18].

ii The sub-mechanism of the oxidation of methanethiol (CH_3SH), present in trace amounts in biogas, but also an important intermediate in CH_4/H_2S oxidation, was taken from the recent work of Gersen et al. [11]. CH_3SH decomposition reactions were updated through RMG rate rules [30].

iii Carbon disulfide (CS_2) and carbonyl sulfide (COS) sub-mechanisms were taken from the modeling works of Glarborg and coworkers [31,32].

Thermodynamic properties were taken from the database of Burcat and Ruscic [33] and RMG database [30]. The complete mechanism includes 141 species and 2224 reactions, and is available as Supplemental Material (SM) in CHEMKIN format, along with thermodynamic and transport properties. In order to assess its generality features, a wide-range validation against the available literature data is shown in the SM, too.

3. Results and discussion

3.1. Experimental results

Considering the compositions listed in Table 1, Fig. 1 shows the experimental profiles of fuel, oxidizer and main reaction products, as well as their related kinetic modeling predictions. It is important to highlight that simulations results are shown only when steady-state conditions are attained. In lean and stoichiometric conditions, after the onset of CH_4 oxidation, a dynamic behavior, i.e. an oscillating combustion with repeated extinctions and ignitions, was often observed: this is a well-known phenomenon in well-stirred reactors [22], whose chemical roots had been previously investigated [34,35]. Yet, in the present work, the oscillating behavior was predicted by the model but not observed experimentally: indeed, oscillations are highly sensitive to the kinetic rates of the termination reactions, thus the range of temperatures where they occur might not always be caught.

When analyzing the experimental and predicted consumption trends of the two fuels, two important observations can be made. First of all, in spite of the small amounts (500 ppm), the addition of H_2S to CH_4 causes an anticipation of CH_4 oxidation onset at all the Φ values. This is not immediate to be identified through the experimental points, due to their resolution (25 K) and their uncertainty (±10%). Such a difference is instead easier to be quantified through model predictions: considering 10% conversion of CH_4 as a reference, the predicted onset is anticipated by 40 to 75 K, with higher values under lean conditions. Apparently, the addition of H_2S slows down the conversion rate of CH_4, occurring over a wider temperature range, instead of the usual abrupt consumption observed with the pure fuel, observed in this work as well as in previous ones [22]. For all the datasets, the kinetic model is able to reproduce the experimental trends of CH_4, reaction products and C_2 intermediates reasonably well. A slightly early onset (~30 K) in the oxidation is predicted in both pure CH_4 and CH_4/H_2S mixtures, which can be observed for intermediate products, too. Apart from that, the shape of the curves is reproduced very well for all the species.

The second point to be raised is the earlier oxidation of H_2S compared to CH_4. All the H_2S profiles share a common inception temperature at 650 K, regardless of Φ value. In leaner conditions (Φ = 0.5) a small conversion (~20%) is measured when transitioning from 500 K to 700 K. As already previously observed with pure H_2S [24], this might be due to residual wall effects, persisting after the treatment described in Section 2.1. However, the temperature at which H_2S reaches 50% conversion ($T_{50\%}$) is comparable for the 3 cases. The kinetic model is able to predict both the inception temperature for Φ = 1 and 2, and $T_{50\%}$ for H_2S for all the datasets reasonably well, and the same holds for SO_2 trends. The H_2S conversion rate through the temperature range is also well predicted, except at Φ = 2, where the model predicts a slower conversion rate at higher temperatures, differently from what experimentally detected. However, with the current mechanism there is no way to explain this deviation, at the same time retaining the physical meaning of the reaction rates and the predictive features of the mechanism (i.e. in a wider range of operating conditions, as shown in the SM).

It is very interesting to notice that this is not the first time that such effects were experimentally observed for CH_4/H_2S mixtures: in their work, Colom-Díaz et al. [12] showed that, in two different FR configurations, the presence of H_2S caused an anticipation in the onset of CH_4 oxidation, too, at atmospheric as well as high-pressure conditions, although occurring, in the pure-fuel case, at much higher temperatures (≥ 1300 K). Similarly, at atmospheric pressure, H_2S consumption in the presence of CH_4 was distributed over a wider range of temperatures, compared to the pure-fuel case. On the other hand, the onset of H_2S oxidation always occurred at similar temperatures as the pure-fuel case, as can be noticed also by comparing the present results with the previous work by Stagni et al. [24] under lean conditions.

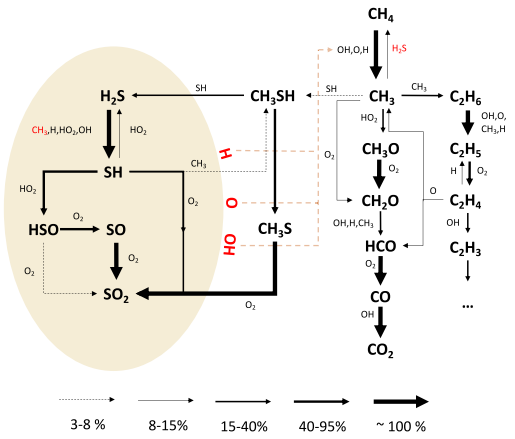

Fig. 2. Carbon and sulfur flux analysis, respectively, in the oxidation of 500 ppm H_2S and 2% CH_4 in JSR (T = 900 K – Φ = 0.5). Flux intensity is related to the single molecule.

3.2. Kinetic analysis

In order to unravel the couplings between the two fuels, flux analysis was carried out for sample conditions, i.e. at the onset of CH_4 oxidation (~10% conversion) at Φ = 0.5 (Fig. 2).

Qualitatively, both CH_4 and H_2S follow the conversion paths, which can be observed for the pure fuels at such relatively low temperatures [22,24]. The coupling, and thus the mutual interaction, occurs at three different levels: (i) first of all, the oxidation process of H_2S, starting in pure conditions at temperatures much lower than CH_4 (700 K vs at least 1000 K) and converting the fuel to SO_2, acts as a pool of OH, O and H radicals. As a result, they become available for H-abstraction from CH_4, thus forming CH_3 and triggering its parallel oxidation. (ii) At the same time, the second interaction is generated by the mutual H-abstraction (CH_3+H_2S → CH_4+SH): indeed, the formation of CH_3 through the dynamics just described enables a further H-abstraction by the same radical, from H_2S itself. This further boosts the oxidation of H_2S, contributing to an earlier conversion. (iii) Third, the process is slowed down by the formation of CH_3SH through CH_3 and SH recombination (written as a decomposition reaction in the current mechanism), which subtracts SH radicals from H_2S oxidation path.

Such couplings find further support in Fig. 3a, showing the reactions driving CH_4 oxidation for variable Φ. In addition to the well-known competitions in the low-temperature oxidation of methane for consuming CH_3 radicals, the SH+HO_2 channel (propagation via HSO+OH vs termination to H_2S+O_2) regulates the reactivity of methane, too, as it sets the radical pool. On the other hand, the recombination of CH_3 and SH inhibits the process, as already said, with an increasing importance at stoichiometric and rich Φ.

This mechanism explains the delayed consumption of H_2S in the presence of CH_4, and is confirmed in the sensitivity analysis to H_2S mass fraction reported in Fig. 3b at its half-conversion temperature (750 K), common for all the Φ values. In addition to the key reaction steps driving H_2S combustion, CH_3 self-recombination and recombination with SH slow down the oxidation process, as they both subtract active radicals from the fuel–fuel H-abstraction, which instead enhances oxidation.

It is also worth highlighting that CH_3O_2 and CH_3O were both shown playing a critical role in the low-temperature oxidation of CH_4. Recently, possible interactions with sulfur-containing species were assessed in literature by Zhang et al. [36], although no full rate constants are provided (thus were not included in the model). In the next future, the inclusion of such reaction pathways in the current model might shed light on their actual importance in the investigated conditions.

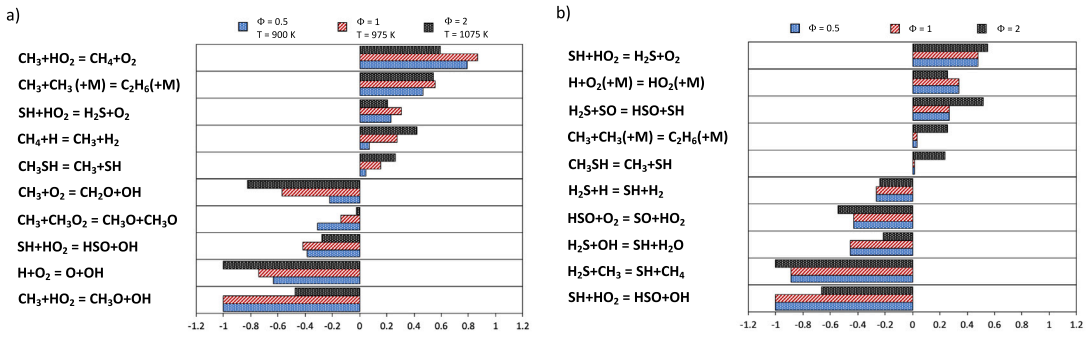

Fig. 3. Sensitivity coefficients to (a) CH_4 mass fraction in the oxidation of 500 ppm H_2S and 2%CH_4 in JSR, at ~10% CH_4 conversion, and (b) H_2S mass fraction in the oxidation of 500 ppm H_2S and 2%CH_4 in JSR (T = 750 K).

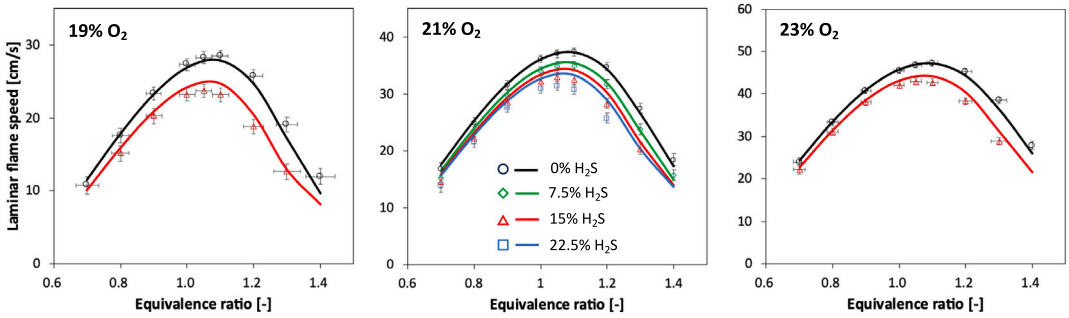

Fig. 4. Laminar flame speed of $CH_4/H_2S/O_2/N_2$ mixtures (P = 1 atm - T_u = 298 K). Experimental data [15,16] and modeling predictions.

3.3. Carbon–sulfur interaction

The analysis of the reaction pathways involved in the low-temperature oxidation of CH_4/H_2S pointed out that carbon–sulfur interaction occurs indirectly at a radical pool level as well as directly at a fuel radical level. In order to assess the generality of the kinetic framework as well as to obtain general conclusions to address future activity, their combined effect was further investigated in flame propagation conditions. As pure fuels, H_2S flames propagate faster than CH_4 ones. Yet, recent experimental works [14–16] have highlighted the slower flame speeds of CH_4 blends with small amounts of H_2S. The role of carbon–sulfur interaction in flame propagation was then unraveled through a comprehensive analysis of $CH_4/H_2S/O_2/N_2$ flames, on the wake of what experimentally done by Han et al. [15,16]. Fig. 4 reports the experimental measurements at ambient conditions, and the related predictions obtained through the developed kinetic mechanism, for variable O_2 mole fraction and H_2S amount in the fuel blend.

For all the O_2 amounts, the modeling predictions confirm the experimental trends with a reasonable accuracy and a slight overestimation for the highest amounts of H_2S. A progressive reduction of the flame speed value with the addition of H_2S is observed, although such decrease tends to flattening, and a maximum inhibiting effect with a successive increase of LFS is expected to be reached for further H_2S additions. This is opposite with respect to what observed in the JSR case: in order to untangle this, sensitivity analysis was performed, and sensitivity coefficients with respect to H mass fraction were calculated in correspondence of the flame front, anchored at the center of the computational grid. For the sake of compactness, Fig. 5 shows only the reactions involving C-S interaction are shown, in addition to a subset of most relevant CH_4-related reactions used as reference values.

In addition to the CH_3 termination to CH_4, a key role is played by its recombination to CH_3SH. As in the low-temperature conditions, this step inhibits the reactivity by absorbing reactive SH radicals. Because

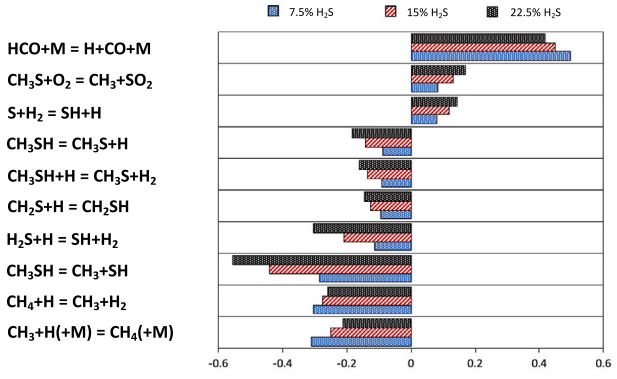

Fig. 5. Sensitivity coefficients of the most relevant reactions to H mass fraction in the laminar flame propagation of $CH_4/H_2S/O_2/N_2$ mixtures (P = 1 atm – T_u = 298 K – Φ = 1), normalized with respect to the value of $H+O_2 \rightarrow O+OH$.

of this, they are taken away from the branching path $SH+O \rightarrow SO+H$, which combined with the successive step $SO+O_2 \rightarrow SO_2+O$, results in a net $SH+O_2 \rightarrow SO_2+H$, i.e. providing the more reactive H radicals. Above all, Fig. 5 shows that the whole CH_3SH chemistry is actually of primary importance for the overall inhibiting effect: the H-abstraction by the H radical from CH_3SH further decreases the overall reactivity as it consumes reactive H atoms returning less reactive methylthio radical (CH_3S). On turn, the competition between CH_3S oxidation and termination provides a further contribution to set the overall reactivity.

Considering the whole CH_4/H_2S oxidation mechanism, CH_3SH chemistry represents the most critical subset: several of its related rates are indeed based on estimations, and a systematic and high-level theoretical activity has been mostly focused on the related H-abstractions by

the major radicals. In particular, there is a substantial lack of fundamental knowledge on the dissociation reactions (or related recombinations, in the reverse direction) involving CH_3SH, providing CH_3+SH, as well as CH_3S+H and CH_2SH+H. The importance of CH_3SH dissociation both in jet-stirred and flame propagation conditions calls for an accurate temperature dependency for all of the three rates. Moreover, as already pointed out by Van de Vijver et al. [19], it is possible that such recombinations might be in the fall-off regime, rather than in the high-pressure limit. Nevertheless, the available literature rates [19,37], as well as those adopted in this work [30], do not account for the pressure effect. As a matter of fact, high-pressure experiments [11–13] have often shown the largest disagreements with kinetic models. Therefore, fundamental studies framing such a role are desirable for a further improvement and generalization of the kinetic model.

4. Conclusions

In this work, the complex chemical role of hydrogen sulfide in the co-oxidation with methane was investigated through a combined experimental and kinetic modeling methodology. In order to investigate the most kinetically critical (and least explored) conditions where such interactions are established, experiments were performed in a JSR, at low temperatures (450 to 1200 K) and lean-to-rich (0.5 to 2) equivalence ratios. Initial conditions with and without 500 ppm H_2S were considered, in order to assess the net effect of its addition. In parallel, a kinetic model was set up by relying upon previously validated CH_4 and H_2S core chemistry, and including carbon–sulfur interactions, established through mutual H-abstraction, a methanethiol sub-mechanism and carbon sulfides chemistry.

The obtained experimental data showed an anticipated onset of CH_4 oxidation due to the addition of H_2S for all of the investigated conditions. On the other hand, the consumption of H_2S was observed to begin at much lower temperatures (650 K), regardless of the equivalence ratio, yet with a much slower conversion rate with respect to the pure fuel [24].

The kinetic mechanism was able to reproduce the experimental trends for all the species reasonably well, especially under lean and stoichiometric conditions, with an underprediction of H_2S conversion in rich condition and higher temperatures. It provided an insight on the kinetic foundations behind the observed behavior. The higher reactivity of H_2S generates a radical pool (OH, O, H) available for H-abstraction from CH_4 and anticipating its conversion. On the other hand, the H_2S consumption rate was found to be affected by the H-abstraction by CH_3 from the fuel itself, enhancing its oxidation, and negatively by CH_3 termination to CH_3SH, inhibiting the conversion of both fuels.

On the other hand, the sensitizing effect of H_2S on CH_4 oxidation turned into an inhibiting one when considering flame propagation features of the related mixtures. In this case, the whole chemistry of CH_3SH and its decomposition products was found to be crucial, i.e. not limited to its decomposition into CH_3 and SH. As a matter of fact, in spite of its importance in the whole temperature range, this is the most uncertain part from a kinetic point of view, requesting further theoretical focus in the next future to provide a comprehensive fundamental description and consolidating the predictive features of the mechanism.

Novelty and Significance Statement

This manuscript fills an important knowledge gap in the low-temperature interaction between hydrogen sulfide (H_2S) and methane (CH_4), which has not been experimentally addressed in Jet Stirred Reactors so far. From an applicative point of view, this is of crucial significance to get a comprehensive understanding of sour gas and biogas oxidation, which are occupying an increasing share of the energy portfolio. Moreover, this work provides an important step forward towards the development of a kinetic model for CH_4/H_2S oxidation with generality features, i.e. predictive in the whole range of operating conditions, thoroughly describing sensitizing and inhibiting effects of H_2S (not limited to the present dataset, but also extended to different reactors and operating conditions).

CRediT authorship contribution statement

Alessandro Stagni: Contributed to design the research, Developed the kinetic model, Wrote the manuscript. **Suphaporn Arunthanayothin:** Performed the experiments, Revised the manuscript. **Olivier Herbinet:** Designed the experiments, Revised the manuscript. **Frédérique Battin-Leclerc:** Designed the research, Supervised the experimental campaign, Revised the manuscript. **Tiziano Faravelli:** Contributed to model development and design of experiments, Revised the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.proci.2024.105585.

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