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On explosion limits of $H_2/CO/O_2$ mixtures

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ABSTRACT

The pressure–temperature explosion limits of $H_2/CO/O_2$ mixtures were analyzed computationally and theoretically. It is shown that, with the addition of even a minute quantity of H_2, the mixture explosion limits evolve from being monotonic to the non-monotonic Z-shaped response characteristic of H_2/O_2 mixtures. It is further shown that the explosion limit at various conditions can be reproduced well with a reduced mechanism of 12 elementary steps and 10 species. Eigenvalue analysis of this mechanism leads to an analytic solution for the explosion limits, yielding explicit expressions for the degenerate high- and low-pressure explosion peninsulas as well as the individual first, second and third limits. The separate and coupled roles of H_2 and CO oxidation are identified, leading to enhanced insight of this foundational component in the mechanisms of hydrocarbon oxidation, as well as useful information in the utilization of syngas.

1. Introduction

The explosion limits of a given fuel/oxidizer mixture are the pressure–temperature boundaries of the mixture that separate regimes of explosion and non-explosion [1–3]. In particular, the explosion limits of H_2/O_2 mixtures, which exhibit a characteristic Z-shaped curve in the pressure-vs-temperature plot, with the three segments of this curve referred as the first, second and third limits, have been studied extensively [3–6]. Furthermore, it is well established that the first limit is controlled by the gas-phase chain branching reactions competing with radical diffusion to and deactivation at the wall; the second limit by the gas-phase $H–O_2$ branching and termination chain reactions; and the third limit by the gas-phase HO_2 and H_2O_2 chemistry competing with wall deactivation.

The corresponding explosion limits of $H_2/CO/O_2$ mixtures, whose chemistry not only represents the next level of complexity in fuels oxidation, beyond that of the H_2/O_2 chemistry, but it also forms the foundational block of hydrocarbon oxidation, have not been adequately explored. Fundamentally, while the oxidation of dry CO is an extremely slow process such that for all practical purposes it is considered to be un-ignitable, the addition of a minute amount of hydrogen, or a hydrogen-containing species, greatly promotes its reactivity in the role of a catalyst, and the term “catalyzing” has been used to describe this effect in the literature [7–9]. It is thus of interest to explore and quantify the extent of the catalytic effects in response to hydrogen addition, the state of the catalytic saturation with increasing addition, and the subsequent influence of the H_2 chemistry on the overall reactivity of the mixture, particularly in terms of the Z-shaped H_2/O_2 explosion responses. Such a study is also of obvious relevance to the recent interest in the combustion of syngas, which mainly consists of H_2 and CO, as it can be produced through gasification of coal and biomass and used in stationary gas turbines and IC engines [10,11]. Furthermore, it is noted that reactions involved in syngas combustion play an essential role in the hierarchical structure of the oxidation models of hydrocarbon fuels [10]. Compared to hydrocarbons, the oxidation of CO/H_2 mixtures is governed by substantially smaller sizes in terms of the number of intermediate reactions and species. While such small size facilitates the simulation of CO/H_2 combustion, it nevertheless also renders the combustion response to be very sensitive to the individual reactions and species. Consequently, it is crucial for the reaction pathways to be clearly identified for the system.

In view of the above considerations, we shall simulate the explosion limits of $H_2/CO/O_2$ mixtures, with various amounts of H_2 addition, and identify the roles and limits of H_2 catalyticity and its subsequent dominance in terms of the *Z*-curve response at low and high concentrations, respectively. We shall further study the controlling chain branching and termination reactions as related to the separate and coupled chemistry of H_2 and CO oxidation, and derive explicit expressions for the various Z-shaped $H_2/CO/O_2$ explosion limits.

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2. Computation specification

The explosion limits of $H_2/CO/O_2$ mixtures were computed by the SENKIN code [12]. The explosion criterion at a given pressure and temperature is determined by 50 K increments at constant volume and adiabatic conditions. The calculation pressure range was from 3.5 to 3.2×10^7 Pa, and the temperature range was from 300 to 2500 K. Based on uncertainty quantification and comparison of several recent syngas combustion mechanisms [13,14], three chemical kinetic models with performance validations were employed in this study: namely the Kéromnès mechanism of 15 species and 49 reactions [15], the Davis mechanism of 14 species and 38 reactions [16], and the NUIG-NGM syngas sub-mechanism of 15 species and 41 reactions [17]. All the calculations were conducted for the stoichiometric concentrations. As found in previous studies, termination of radicals at wall has a strong effect on the explosion limits [6]. The carriers are destroyed at the wall with a temperature-dependent reaction as $R \xrightarrow{k_R}$ wall termination, where R denotes the radicals H, O, OH, HO_2, H_2O_2 and HCO in the system. The rate of wall termination [1] is given as $k_R = \frac{1}{4} \in v\frac{S}{V}$, where $\in$ is the efficiency of wall destruction, which is usually around 10^{-5} to 10^{-2} for glass and quartz [2] and the value of $\in = 10^{-3}$ is adopted; v is the average velocity of thermal motion of radicals; and S/V is the surface-to-volume ratio and for a spherical chamber $S/V = 3/r$. The radius of chamber is fixed as $r = 37$ mm in this study. As noted in [18], as the efficiency of wall destruction decreases, the effect of species diffusion decreases, and at the condition of $\in = 10^{-3}$, the surface effect is controlled by the surface termination reaction. The percentage of hydrogen in the fuel mixture is defined as $F_{H_2} = C_{H_2}/(C_{H_2} + C_{CO})$, where C_i represents the mole concentration of species i.

3. Results and discussion

3.1. Detailed solutions

The explosion limits of syngas, *i.e.* H_2/CO mixtures, with different H_2 mole fractions calculated with the three selected mechanisms are collectively shown in Fig. 1(a) and (b). In general, the results are qualitatively similar for the three mechanisms. Also, the deviations between the different mechanisms are much smaller for cases of high than low H_2 concentrations. The most severe deviations appear in the intermediate pressure range of 10^3–10^5 Pa.

The catalytic action of H_2 is demonstrated prominently in Fig. 1(b), which shows that while the explosion limit of pure CO is monotonic, it changes to *Z*-shaped with minute quantities of hydrogen addition, say with just 10^{-5} to 10^{-4} H_2 mole fraction in the fuel mixture for the surface deactivation reactions adopted. With further H_2 addition, the explosion limits move towards those of pure H_2.

Although the size of the detailed syngas mechanism is largely computationally accessible, availability of analytic formulas for the explosion limits can help to reveal the controlling parameters and chemical processes involved. The present investigation therefore aims to develop these formulas and provide accurate evaluations essentially equivalent to those found through computation with detailed chemistry. To further assist the analysis, the minimum kinetic reactions need to be identified in order to obtain concise analytical expressions. Consequently we have adopted the reduced mechanism of Boivin et al. [19], which includes 10 elementary reactions. Furthermore, the associated rate coefficients have been updated to the values of the Kéromnès mechanism. Furthermore, since the HO_2+H reactions, namely $HO_2 + H \rightarrow H_2 + O_2$ and $HO_2 + H \rightarrow 2OH$, as well as the HCO related reactions are only important for flame speed simulations, they are not included in the mechanism. The resulting 10-step reduced mechanism, consisting of eight H_2–O_2 related reactions (R1–R8) and two CO related reactions (R9 and R10), is listed as R1 to R10 in Table 1.

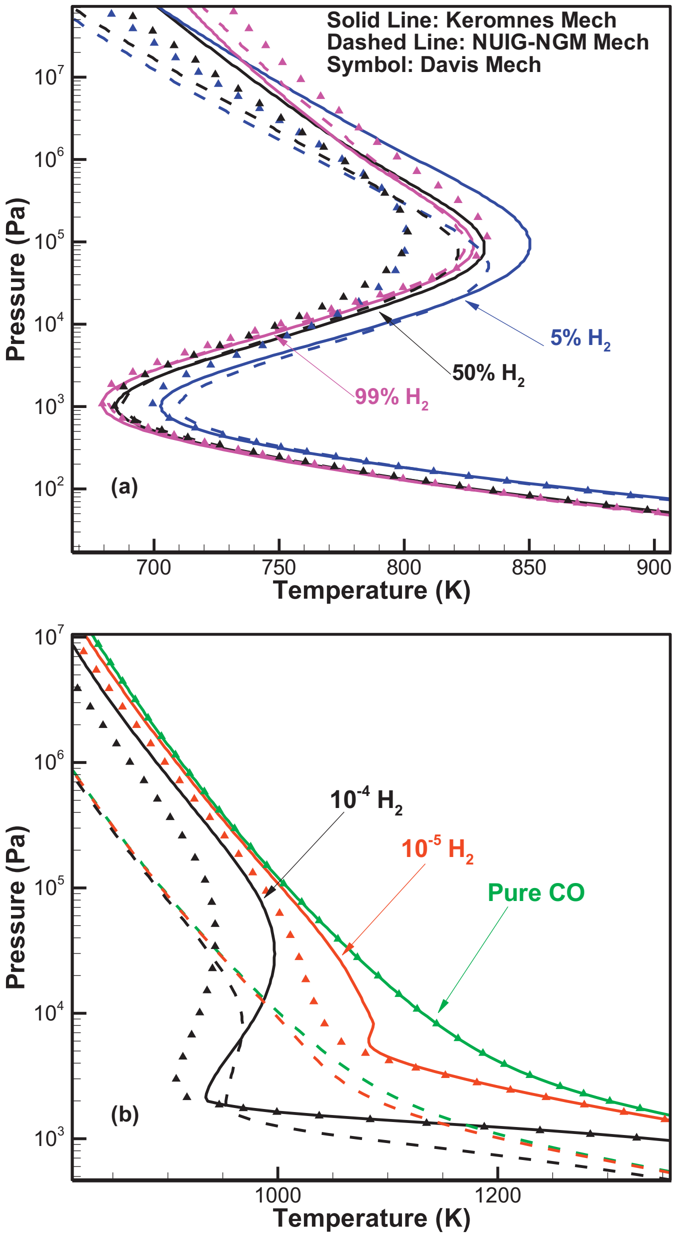

Fig. 1. Explosion limits of stoichiometric $CO/H_2/O_2$ with different kinetic mechanisms.

Figure 2 compares the simulation results based on this simplified mechanism of R1 to R10 and the detailed mechanism. It is seen that when the hydrogen percentage in the fuel is larger than 10%, the reduced mechanism agrees well with the detailed mechanism. However, for cases with 5% and 1% H_2 in the fuel mixture, the reduced mechanism shows larger discrepancies with the detailed mechanism, especially at the second and third limits. Furthermore, while the detailed mechanism shows sensitive response of the second limit to changes of the fuel mixture, there is no such sensitivity for the reduced mechanism. To resolve such a discrepancy, we have added the following two reactions involving CO oxidation from the Kéromnès mechanism: R11: $CO + O\ (+M) \rightarrow CO_2\ (+M)$ and R12: $CO + O_2 \rightarrow CO_2 + O$, recognizing that they must be essential to the explosion limits of pure CO as they are the reactions without the presence of hydrogen.