

Chemical Kinetics Illustrations: Methane and Hydrogen Sulfide Combustion

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Abstract

Methane combustion has to be one of the most studied systems but nevertheless because of the dependence of many of the rates of elementary reactions in the mechanism on pressure and temperature (unimolecular or chemically activated reactions) as well as combustion conditions, fuel-rich or lean, discrepancies can always be found between two close but different combustion mechanisms authored by different investigators (both in the kinetic coefficients of reactions as well as the results of modeling). Nevertheless, the major chemical pathways are well known.

Keywords: Chemical reaction; Chemical kinetics

Introduction

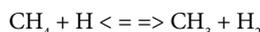
Methane combustion model assembly

In this section an attempt will be made to present the approach to developing the major features for the combustion of methane based on the concepts presented in previous chapters. The starting point is the understanding that methane combustion involves (1) a chain reaction mechanism and (2) that its chemistry obeys the Hierarchical structure of Hydrocarbon combustion.

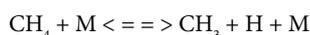
It must be kept in mind that the mechanism that is assembled must explain the overall reaction for combustion of methane or,

$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ (CO, H₂ as well, depending on stoichiometry)

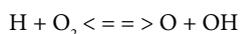
Thus, the initiation of methane combustion involves the attack by small radicals present in the flame or for example in a fuel-rich flame,



Other reactions would involve the attack by OH, O radicals depending on combustion conditions. The formation of such small radicals are initiated by the high temperature decomposition of the fuel or,



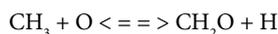
Another important reaction in chain mechanisms is branching or,



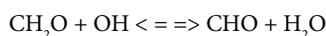
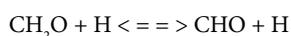
The mechanism must know explain the formation of intermediates such as CO and even C₂ hydrocarbons in fuel-rich flames.

The fate of the methyl radical is most important since it can lead to formaldehyde formation or C₂ hydrocarbon intermediates.

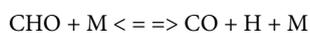
The formation of formaldehyde is as follows,



CH₂O leads to the formation of carbon monoxide by small radical attack,

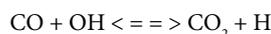


Then,



Carbon monoxide oxidation by OH leads to the final product of

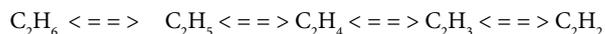
combustion carbon dioxide.



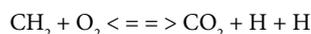
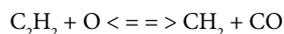
As mentioned above the formation of C₂ intermediates is an important event in fuel-rich flames. Methyl radical again plays an important role,



Then by a sequence of reactions involving the small radicals H, OH, O, and molecular Oxygen O₂, ethane is broken down to C₂H₂ (acetylene) first and finally to CH₂ radical species or,



Acetylene C₂H₂ leads to CH₂ and then CO,



A flowchart for C1/C2 Hydrocarbon oxidation from Warnatz [1] is shown in Figure 1 as a summary of the discussion.

A very well known Methane combustion mechanism consisting of hundreds of reactions for methane including formation of NO_x species is the GRI Mechanism 3.0 which is included in Appendix 2 as an illustration.

Hydrogen sulfide combustion model assembly

The combustion of Hydrogen sulfide [2] follows similar principles as methane discussed above: chain reaction mechanism and thermal decomposition of the fuel as radical initiation reaction. The overall reaction is:

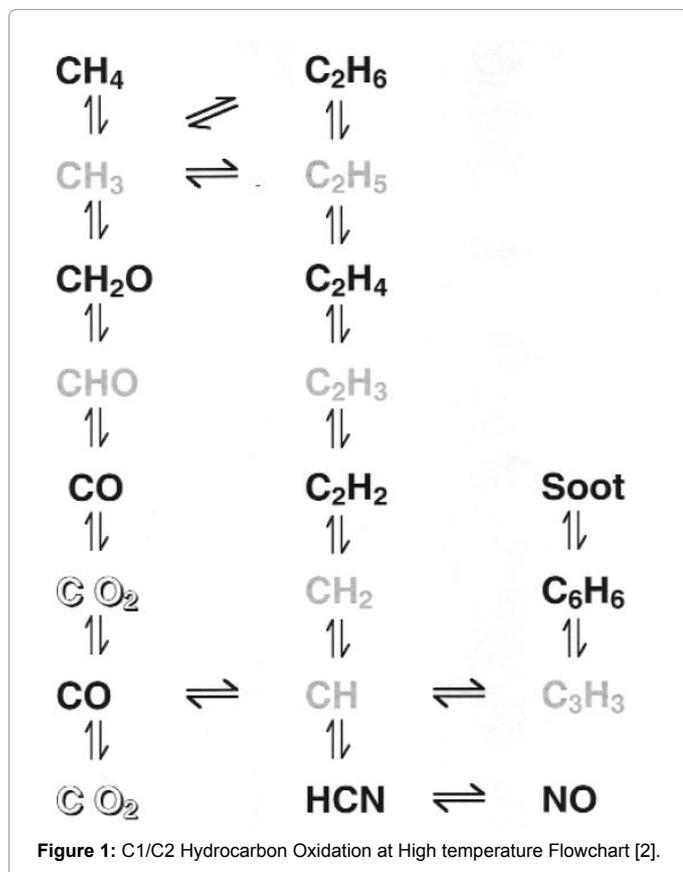


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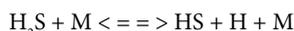
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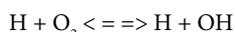


The mechanism needs to explain the formation of SO_x and S_x depending on stoichiometric conditions.

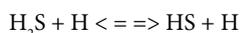
The formation of small radicals is initiated by the high temperature decomposition of H_2S or,



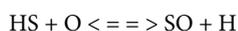
Most important also is chain branching:



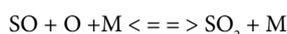
Under fuel-rich conditions the main path for decomposition would be



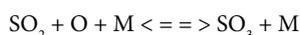
The formation of oxygenated species starts with,



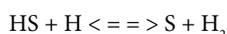
Then



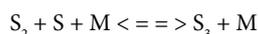
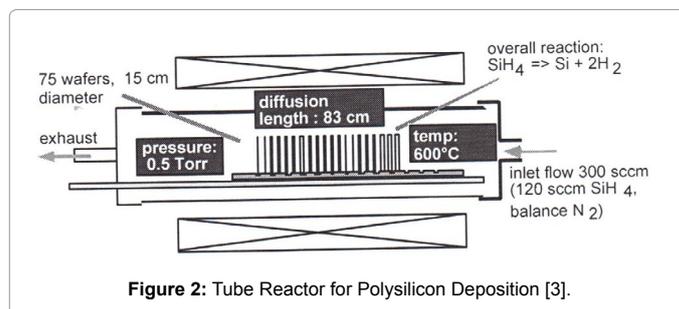
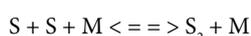
Under fuel-lean conditions SO_3 can be produced by the reaction.



The formation of Sulfur vapor can be explained by the following reaction,



Molecular growth of the Sulfur species then takes place by radical addition reactions,

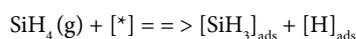


Appendix 3 illustrates a combustion mechanism for Hydrogen sulfide under reducing conditions including the formation of S_2 or sulfur vapor species [2].

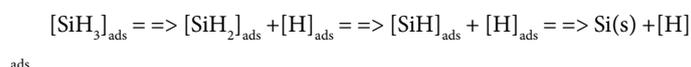
Chemical vapor deposition: polycrystalline silicon

This example is attributed to Dobkin and Zuraw [3]. The reaction mechanism for deposition of polycrystalline Silicon from Silane in the gas phase on silicon wafers is presented. See Figure 2 for the experimental set-up, consisting of a plug flow reactor operating at 600°C and 0.5 torr. The temperature of the gas is high enough for radicals to possibly play a role in reactions in the gas phase (not discussed here).

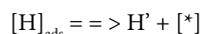
The first step is the chemisorption of silane, SiH_4 (g), onto the surface of the wafer or,



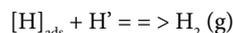
Where $[*]$ is an active site on the surface, it could consist of a dangling bond. This reaction is followed by the rapid decomposition of adsorbed SiH_x to $Si(s)$



As Dobkin and Zuraw point out, the desorption of hydrogen turns out to be complex and rather counterintuitive. Instead of neighboring H atoms getting together to form an H_2 molecule which desorbs, desorption takes place in two steps. First, a hydrogen atom is promoted into a fast-moving weakly-bound (H') but still adsorbed localized surface atom H' or,



The delocalized hydrogen atom then wanders along the surface until it reacts with a surface hydrogen to form molecular hydrogen H_2 ,



References

1. Warnatz J (2000) Hydrocarbon Oxidation High temperature Chemistry. Pure Appl Chem 72: 2101–2110.
2. Gargurevich IA (2005) Hydrogen Sulfide Combustion: Relevant issues under Claus Furnace Conditions. Ind Eng Chem Res 44: 7706–7729.
3. Dobkin DM, Zuraw MK (2003) Principles of Chemical Vapor Deposition.