Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 131 (2008) 483–488

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The directed relation graph method for mechanism reduction in the oxidative coupling of methane

Yuxuan Xin, Zhejian Song, Y.Z. Tan, Dezheng Wang *

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract

A detailed mechanism comprising the GRI-Mech natural gas combustion mechanism and recent updates to it that included soot formation and reactions involving acetylene by Frenklach and coworkers was chosen to describe the gas phase reactions in the oxidative coupling of methane (OCM). The complete mechanism was reduced for use under OCM conditions with the directed relation graph method. The mechanism reduction achieved reduction ratios of 0.55 for the number of species and 0.57 for the number of reactions when the differences in the concentrations of CH_4, O_2, C_2H_6, C_2H_4, and C_2H_2 between the original and reduced mechanisms were required to be less than 5%.

Keywords: Mechanism reduction; Detailed kinetics mechanism; Oxidative coupling of methane; Directed relation graph

1. Introduction

Methane will be a crucial feedstock for the chemical engineering industry and source of energy in the 21st century. It can be utilized in a variety of strategies, such as synthesis gas production followed by Fischer-Tropsch synthesis or the synthesis of methanol, oxidative coupling to ethene, and non-oxidative conversion to aromatics [1]. As a potentially important direct method of methane utilization, the oxidative coupling of methane (OCM) has been well researched with respect to the development of better catalysts and more effective operating conditions. But the process has not been able to achieve economically attractive yields, and it appears that process coupling with another process will be necessary to improve the economics.

As compared to extensive experimental studies, simulation studies can save much cost and permit the investigation of situations that are difficult to use in the laboratory, e.g. process coupling and conditions of high temperature and pressure. Moreover, simulations can give insights into the interactions between microscopic physical and chemical phenomena. It is expected that a multiscale simulation that combines computational fluid dynamics and chemical kinetics can supply valuable information for experimental studies. Therefore, the accurate simulation of an industrial reactor for OCM is significant from both the fundamental and practical standpoints.

Detailed kinetic mechanisms differ from macroscopic kinetics in keeping explicit the descriptions of the chemical behaviors of reaction intermediates and the use of elementary reactions. It has a more solid foundation because it does not make indiscriminate simplifications, e.g. using the concept of a rate-controlling step without being explicit about the reaction conditions for its validity. Due to increased computing power, it is now possible to choose to begin with detailed kinetic mechanisms as the kinetic model. However, because detailed kinetic mechanisms usually include thousands of reactions and up to hundreds of species, their direct implementation in reactive flow simulations is still prohibitively expensive. One still has to use reduced mechanisms developed through mechanism reduction algorithms.

However, in contrast to the conventional use of a macroscopic rate expression, the advantage in beginning with the detailed kinetic mechanism is that the reduced mechanisms are in-house developed and validated with the full mechanism for the relevant reaction conditions. One can perform the mechanism reduction oneself instead of being forced to accept the reduced mechanisms of other researchers, which may have been validated for quite different reaction conditions. Usually a

---

* Corresponding author.
E-mail address: wangdz@flotu.org (D. Wang).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.10.065

user of a reaction mechanism has more specific reaction conditions and product species of interest and desires a more specific precision requirement, e.g. that the differences in the concentrations of a number of chosen species between the original and reduced mechanisms be less than a fixed percentage for his particular reaction conditions. Various reaction mechanism reduction algorithms that reduce detailed chemistry mechanisms subject to user requirements are now available. These are due to much work in developing methodologies for systematic mechanism reduction, and have been recently reviewed by Tomlin et al. [2], Okino and Mavrovouniotis [3] and Law et al. [4].

Mechanism reduction methods can be classified into three major categories: lumping, time scale analysis, and skeletal reduction. Lumping is most useful when there are groups of many reactants or products that have nearly the same chemical behavior, and each group can be treated as one pseudo-species. This is expected to be of limited use in the OCM reaction. Time scale analysis uses various methods to find the highly reactive species or fast reactions in a reacting system, and approximate these as quasi-steady state species and partial equilibrium reactions. The corresponding differential equations are thus replaced with algebraic relations that can be solved explicitly to reduce the number of variables. The intrinsic low dimension manifold method [5] and computational singular perturbation method [6–8] are two systematic approaches of time scale analysis.

In contrast, skeletal reduction is the elimination of species and reactions that are unimportant under the particular reaction conditions of the application. One skeletal reduction strategy is sensitivity analysis, which is one of its earliest methods [8]. Principal component analysis makes use of the Jacobian matrices to analyze species coupling to decouple different reaction groups [9,10]. Bendtsen et al. [11] introduced a time-dependent reaction matrix P whose elements P_{ij} are the production rates of species j from reactions with species i at time t to analyze the chemical dynamics. Interactions between species were quantified by the matrix and for a set of pre-chosen concentrations of the major reactants and products, species that contributed less than a certain percentage to the annihilation or production of these major species were removed. Recently, Lu et al. [12–14] proposed a similar species selection procedure, called the directed relation graph (DRG) approach, and applied it to the automatic generation of skeletal mechanisms from detailed chemistry mechanisms. In this work, we used the DRG approach developed by Lu et al. to simplify the gas phase reactions of OCM to a skeletal mechanism for the reaction conditions of OCM.

2. Directed relation graph (DRG) method

The DRG method was proposed by Lu et al. [12–14] to reduce large detailed mechanisms. It uses a (mathematical) graph, called the DRG, which comprises the set of directed paths that mark the species that will remain in the skeletal mechanism (all the coupled species, in the terminology of Lu et al.). The species of the skeletal mechanism are defined (see below) as those that occur in reactions that are significant for the production of the various user-specified species that were experimentally measured. The DRG for a particular reaction mechanism is constructed by first specifying the vertices of a graph to represent the species present in the mechanism. Each vertex (species) is considered in turn to compute the set of reaction rates (for the reaction conditions of a sampled point) of all the reactions in which that species takes part. The rates in the set are summed. Then, the significant reactions of the set are recognized by the criterion that these are reactions with a ratio of its rate to the summed rate of all reactions that produce species A, named r_{AB}, is larger than a user specified small threshold relative error ε [12–14]. The significant reactions are retained as directed edges originating from species A. A program based on the pseudo-code program in Lu and Law [13] and the graph representation and depth first search algorithm in Cormen et al. [15] was used in this work.

The program lets users specify a set of target species A_i. For each target species, the algorithm identifies those species that are significant in its production (depletion is included as negative production) as specified by the value of ε, and whose removal will result in computed concentrations of the target species that will exceed ε. This is done by directed paths as described above. Then, all these species are collected by a standard graph search (depth first search or breadth first search [15]) of the DRG. The union of these species is retained to comprise the species (and reactions) of the skeletal mechanism. In order to ensure that the skeletal mechanism is suitably representative of a specific simulation, the reaction conditions for which the reduced mechanism is to be used have to sufficiently sampled, that is, the final skeletal mechanism is the union of the species (and reactions) of the skeletal mechanisms of very many pressure, concentration, and temperature values in the simulation pressure, concentration, and temperature ranges. The above algorithm for the construction of a DRG of a certain set of reaction conditions is repeated to construct the DRGs of the reaction conditions of all sampling points, and the species retained to comprise the skeletal mechanism is the union of the retained species of each point. The DRG construction and selection of retained species and reactions depend on one user-defined parameter ε.

3. Detailed gas phase reaction mechanisms for OCM

Quite a number of detailed gas phase reaction mechanisms for OCM have been developed by different researchers [e.g. 16–22], and there are also many gas phase methane combustion mechanisms [e.g. 23–26] that can be relevant, and a difficult choice in a work on OCM now is the choosing of the best mechanism from the many detailed gas phase reaction mechanisms available. Unfortunately, although all these are ostensibly detailed chemistry mechanisms, they are not elementary reaction mechanisms in the strict sense of the concept of elementary reactions, that is, their kinetic parameters should not be patchwork inter-changed. For example the authors of GRI-Mech [23] have recommended that all their kinetic parameters be used as a whole set because they have ‘‘been optimized as a whole’’. Due to this, that is, the building of a more comprehensive mechanism by patchwork means from all the available detailed chemistry mechanisms is not advisable at this time, the merits of the different mechanisms were compared as whole sets.

It can be noted here that many of the gas phase reaction mechanisms for OCM were developed 25 years ago and all are more than 10 years old, and that in the meantime, several excellent reaction mechanisms from workers in combustion science have been introduced for describing natural gas combustion. Thus, one aspect of the work here was to examine the merits of the existing mechanisms and to see if a contemporary mechanism from the associated field of combustion science can be used as an update of the gas phase reaction mechanism of OCM.

In studies specific to the OCM reaction, in the 1980s, McCarty and coworkers developed a reaction mechanism consisting of 27 chemical species and 140 elementary reactions [17] based on free radical chemistry, and Van der Wiele et al. reported a kinetic model of over 164 elementary reactions [18] from the regression of their own methane–oxygen homogeneous reaction data. In 1994, Mims et al. [19] proposed a detailed chemical mechanism comprising 450 reversible elementary reactions and 115 species that was based on the detailed isotopic analysis of the products of the oxidation of $^{13}CH_4$–$^{12}C_2H_4$ mixtures, which was recently also used by Green and coworkers [20] to develop an upper bound on the yield from OCM. Further mechanisms are also those from the groups of Marin [21] and Baerns [22].

From studies on natural gas combustion that should be highly relevant to the OCM reaction, mechanisms are available from the groups of Frenklach and coworkers [23], Côme and coworkers [24], Pilling and coworkers [25], and Williams and coworkers [26]. These mechanisms were originally developed for fuel-lean conditions, and this may be the reason why they had not been considered for use in OCM. However, recent updates [27–29] that focused on soot formation in flames and the reactions involving acetylene have extended the GRI

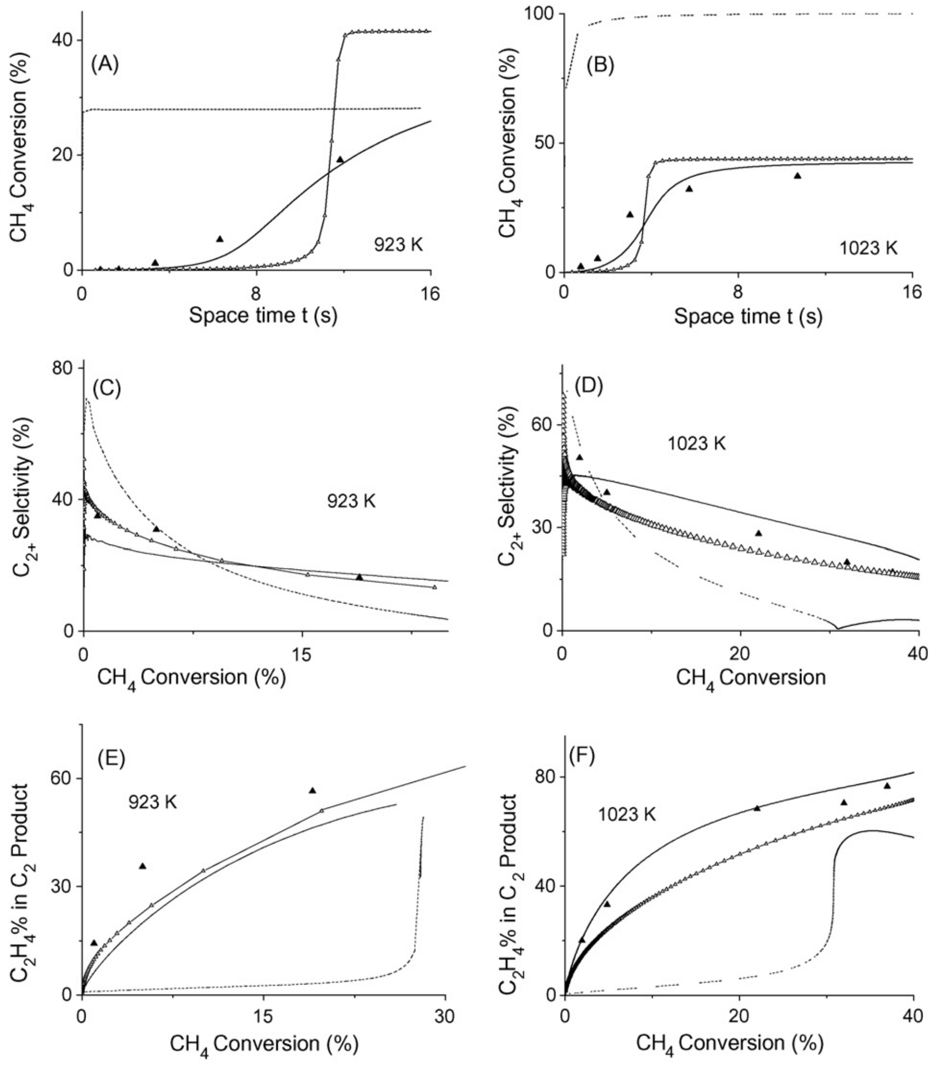

Fig. 1. Comparison of homogeneous CH_4 oxidation data with the simulations using various mechanisms. Triangles are experimental data at the indicated temperatures and a feed of $P(CH_4) = 0.47$ atm, $P(O_2) = 0.23$ atm, $P(Ar) = 0.3$ atm. The curves are simulations with the McCarty mechanism (dashed curves), Mims mechanism (solid curves), and GRI-Frenklach mechanism (connected small symbols).

mechanism to fuel-rich conditions, and its present comprehensiveness and updated data make it attractive for describing the gas phase reactions in the OCM reaction. Here, we shall call this the GRI-Frenklach mechanism [23,27–29]. Thus, this advance made in the mechanism of methane combustion in the years since the high tide of OCM research in the 1990s makes it pertinent to begin with an evaluation of which is presently the most reasonable detailed gas phase mechanism to use for the OCM reaction.

In order to compare the merits of the various gas phase mechanisms, this work chose the homogeneous CH_4 oxidation data reported by Wolf [16] and the homogeneous CH_4 oxidation data reported by Van der Wiele et al. [18] as the basis of evaluation. Actually, the use of the data of Van der Wiele et al. would automatically create a bias towards the Van der Wiele mechanism, and another criterion described below was used to examine the merit of the Van der Wiele mechanism, and also the Marin [21] and Baerns [22] mechanisms. The various mechanisms were used to simulate the homogeneous CH_4 oxidation data from Wolf [16]. The comparison of experimental data with the simulations using some selected different mechanisms is shown in Fig. 1 (the simulations of the other mechanisms are not shown to avoid cluttering). The results showed that the simulations using the mechanisms developed by Mims et al. [19] and GRI-Frenklach [23,27–29] agreed best with the experimental data, and on this basis, they should be considered equally good.

The mechanism developed by McCarty failed to correctly simulate the experimental results of Van der Wiele et al. [20] and Wolf and coworkers [16]. The other natural gas combustion mechanisms, namely, those by Côme and coworkers [24], Pilling and coworkers [25], and Williams and coworkers [26] were not meant for use under fuel-rich conditions, whereas it can be expected that during OCM, oxygen adsorption will be much faster than methane adsorption and there will be a highly fuel-rich gas phase in the OCM reaction. Actually, it was the recent updates [27–29] that extended the GRI mechanism to fuel-rich conditions that made it possible to consider it for the OCM reaction. For a similar reason, the simplifications of the GRI mechanism available [23] could not be considered for use here because they lacked the reactions that lead to aromatic species and soot, whereas these reactions are expected to be significant in leading to catalyst deactivation.

Broadly speaking, the simulations using the Van der Wiele mechanism and also the Marin [21] and Baerns [22] mechanisms were spotty, and also for the following reason, it was decided not to use these. The mechanism data of Van der Wiele et al. [20] gave the kinetic parameters separately for the rates of forward and reverse reactions, which then can be used to calculate the reaction equilibrium constant by taking the quotient of forward rate constant by reverse rate constant. For every reaction in the reaction list in the Van der Wiele mechanism, the equilibrium constants were compared with the corresponding equilibrium constants calculated using the GRI database [23]. It was found that in most cases, the quotients of the forward rate constant by the reverse rate constant were different from the same reaction equilibrium constants calculated using the GRI database. We took this to mean that the kinetic parameters in the reactions in the mechanism of Van der Wiele were not those of an elementary reaction mechanism, but implied that they were fitted parameters that should be restricted in their use to the conditions of the experimental data used to deduce them. This made the Van der Wiele mechanism less attractive. For the same reason, the Marin [21] and Baerns [22] mechanisms were also less attractive.

Neither the mechanisms of Mims et al. nor GRI-Frenklach could be discriminated against by the homogeneous CH_4 oxidation data shown in Fig. 1. Also, since either one comprised about 100 chemical species and 400 elementary reactions, it was impractical to seek to perform a discrimination test using the kinetic parameters of all the individual elementary reactions. Thus, the subsequent discrimination was performed using the smaller number of reactions of their skeletal mechanisms obtained with the mechanism reduction aid of the DRG method. The mechanism reduction of the GRI-Frenklach mechanism is described below. Here, we use the results to discuss the choice of the gas phase mechanism for the OCM reaction.

Since skeletal mechanisms only keep the important species and reactions, it is reasonable to believe that the differences between the skeletal mechanisms of Mims et al. [19] and GRI-Frenklach [23,27–29] will account for the main differences between their complete mechanisms. With the use of the DRG method, these two mechanisms were reduced to skeletal mechanisms comprising 21 and 23 species, respectively. The comparison between them is given in detail in Appendix A. Broadly speaking, the two skeletal mechanisms have almost the same set of species and most of their reactions, which explains why the simulations using these two detailed mechanisms agreed well with each other. It is likely that they were developed from the same database. On the consideration that the GRI-Frenklach mechanism includes more reactions on the behavior of oxygen-containing intermediates and reactions that produce soot (which will be important in simulating catalyst deactivation), and had been updated recently [27–29], this is the mechanism that we recommend for describing the gas phase reactions in present works on the OCM reaction.

4. Skeletal mechanism of the GRI-Frenklach mechanism

A mechanism, GRI-Frenklach, comprising 71 species and 486 reactions that was based on GRI-Mech 3.0 [23], and the papers of Wang and Frenklach [27], Appel et al. [28], and Eiteneer and Frenklach [29], was used to describe the gas phase reactions of the OCM reaction. The N containing elementary reactions in GRI-Mech 3.0 were not used because for environment protection, there is an incentive to avoid creating NO_x pollutants and it can be assumed that there was no N_2 in the OCM feed. If air is used for the OCM reaction, then these reactions will have to be added back. However, it can be noted that it is not economical to use air in OCM because it will cause a recycle load problem. Simulations using an isothermal and constant pressure (near 1 atm) plug flow reactor at different temperatures and ratios of CH_4/O_2 were used as the data source for the reaction conditions of the sampling points of the

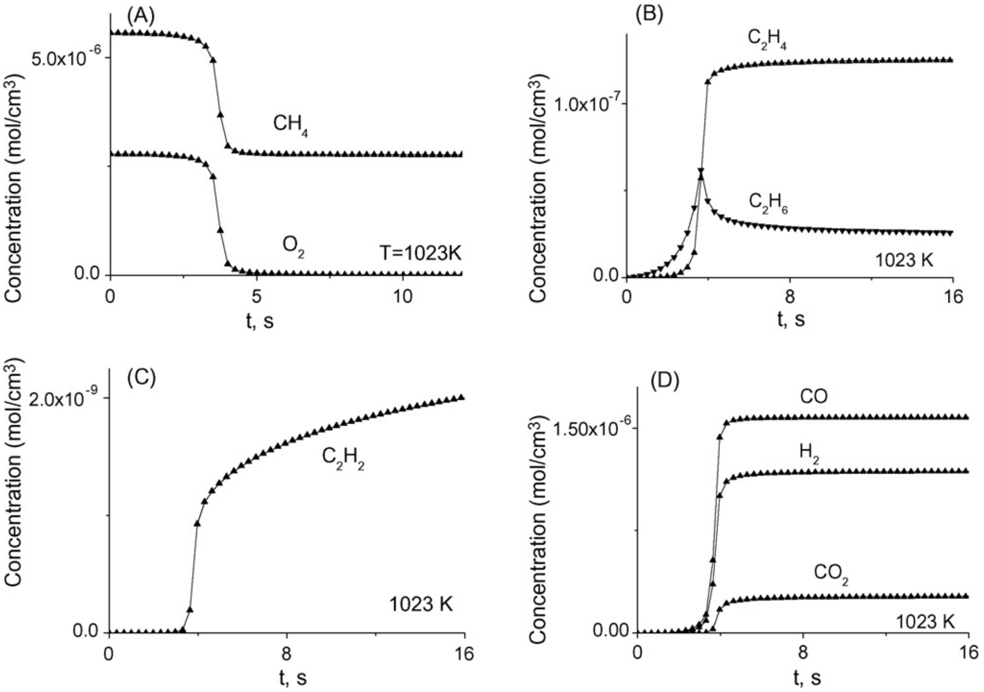

Fig. 2. Comparison of species concentration profiles as a function of space time *t* calculated by the complete (solid curves) and DRG-reduced mechanisms (triangles). The simulation condition was: temperature = 1023 K, $P(CH_4)$ = 0.47 atm, $P(O_2)$ = 0.23 atm, $P(Ar)$ = 0.3 atm.

mechanism reduction. CH_4, O_2, C_2H_6, C_2H_4, and C_2H_2 were selected as the target species, and their concentrations were required to have less than 5% differences from those of the complete mechanism. The choice of the plug flow reactor was dictated by that the DRG method depends on a representative sampling and a simulation that can be performed quickly was needed to establish the reaction conditions that are likely to exist during the OCM process.

The detailed mechanism comprising 71 species was simplified by the DRG method to the reduced mechanism consisting of the 39 species shown in Appendix A. A consideration of the saving in computing time for a computational fluid dynamics (CFD) simulation will depend on the type of simulation. However, it can be assumed that if mechanism reduction is involved, it is likely to be a reactive flow simulation where the solution of the chemical kinetics is the most expensive part of the calculation. For stiff chemical kinetics, the problem will be dominated by the computation of the Jacobian and the convergence rate of the iterative solution method, and the CPU time required can increase proportionally to the square of the number of species. However, in computationally intensive problems, a researcher will also alternatively consider methods that maintain just enough precision only in the species of interest, take advantage of the structure of the kinetics to reduce or eliminate stiffness, and use sparse matrix techniques to keep the CPU time required linearly proportional to the number of species [30]. Thus, the CPU time required can be proportional to the first to second power of the number of species. In our work, the reduced mechanism usually costs 30% CPU time of the detailed mechanism.

The comparison of the skeletal mechanism with the complete mechanism for a typical sampling point which is representative of an OCM operation space is shown in Fig. 2. Without showing the data, we comment that this is typical of the sampling points taken for temperatures ranging from 900 to 1100 K, pressures from 0.8 to 1.2 atm, and CH_4/O_2 ratios from 0.4 to 0.6. Fig. 2 shows that the target species concentration profiles calculated by the complete and DRG-reduced mechanisms agree within ‘‘visual’’ accuracy, which indicated that the original detailed mechanism has been successfully reduced.

5. Conclusion

A detailed chemistry gas phase mechanism, the GRI-Frenklach mechanism, was selected for describing the gas phase reactions in the oxidative coupling of methane reaction system. The selection was based on comparing the simulations using different literature mechanisms with literature experimental homogeneous CH_4 oxidation data. The directed relation graph method was applied to reduce the selected detailed mechanism to a skeletal mechanism with only half the number of species of the complete mechanism.

Acknowledgement

We thank the Ministry of Science and Technology of China (No. G1999022408) and the National Natural Science Foundation (China) (No. 20773075) for support.

Appendix A. The species in the skeletal mechanism after reduction by the DRG method

Species of the DRG-skeletal mechanism are described in Table A.1.

Table A.1
Species of the DRG-skeletal mechanism

O_2	H	O	OH	H_2	HO_2
H_2O_2	CO	CH_2	HCO	$CH_2(S)$	CH_3
CH_2O	CH_4	CO_2	CH_2OH	CH_3O	CH_3OH
C_2H_2	C_2H_3	C_2H_4	C_2H	C_2H_6	HCCO
CH_2CO	H_2O	*p*-C_3H_4	*a*-C_3H_4	CH_3CCH_2	C_3H_7
C_3H_8	*a*-C_3H_5	CH_2CHO	C_3H_3	C_4H_2	*n*-C_4H_3
i-C_4H_3	C_4H_4	C_3H_6			

Note: The species symbols used are those of Frenklach and coworkers [23,27–29].

Table B.1
Comparison of the species of the two different skeletal mechanisms

Species shared by the Mims and GRI-Frenklach skeletal mechanisms					
CH_4	H_2	H_2O	C_2H_6	C_2H_3	CH_2O
H	O	O_2	C_2H_5	H_2O_2	HCO
CH_3	OH	HO_2	C_2H_4	CH_3O	CH_2CO
CO	CO_2	C_2H_3O			
Additional species of the GRI-Frenklach skeletal mechanism					
CH_2OH	CH_3OH				

Appendix B. The comparison of the skeletal mechanisms of Mims and GRI-Frenklach

The skeletal mechanisms of Mims and GRI-Frenklach were used to discriminate the suitability of their original mechanisms for OCM simulation. Since the interest was on finding the main difference between these mechanisms, their skeletal mechanisms were obtained with errors on the main species concentrations of 1.5%, and hence their species were less than that shown in Appendix A. The species remaining in the skeletal mechanism of Mims was a subset of those in the skeletal mechanism of GRI-Frenklach. Most of the reactions of the skeletal mechanism of Mims, and their kinetic parameters as well, were the same as those of GRI-Frenklach. The skeletal mechanism of GRI-Frenklach had about 50 more reactions of oxygen-containing species (Table B.1).

References

[1] J.H. Lunsford, Catal. Today 63 (2000) 165.

[2] A.S. Tomlin, T. Turanyi, M.J. Pilling, in: M.J. Pilling (Ed.), Low-temperature Combustion and Autoignition, Comprehensive Chemical Kinetics, vol. 35, Elsevier, 1997 293 pp..

[3] M.S. Okino, M.L. Mavrovouniotis, Chem. Rev. 98 (1998) 391.

[4] C.K. Law, C.J. Sung, H. Wang, T.F. Lu, Am. Inst. Aero. Astro. J. 41 (2003) 1629.

[5] U. Maas, S.B. Pope, Combust. Flame 88 (1992) 239.

[6] S.H. Lam, D.A. Goussis, Proc. Combust. Inst. 22 (1988) 931.

[7] S.H. Lam, D.A. Gousis, Int. J. Chem. Kinetic 26 (1994) 461.

[8] A. Massias, D. Diamantis, E. Mastorakos, D.A. Goussis, Combust. Flame 117 (1999) 685.

[9] S. Vajada, P. Valko, T. Turanyi, Int. J. Chem. Kinetic 17 (1985) 55.

[10] T. Turanyi, New J. Chem. 14 (1990) 795.

[11] A.B. Bendtsen, P. Glarborg, K. Dam-Johansen, Comput. Chem. 25 (2001) 161.

[12] T.F. Lu, C.K. Law, Combust. Flame 146 (2006) 472.

[13] T.F. Lu, C.K. Law, Combust. Flame 144 (2006) 24.

[14] T.F. Lu, C.K. Law, Proc. Combust. Inst. 30 (2005) 1333.

[15] T.H. Cormen, C.E. Leiserson, R.L. Rivest, C. Stein, Introduction to Algorithms, 2nd ed., MIT Press, Cambridge, 2001.

[16] Z. Kalenik, E.E. Wolf, in: E.E. Wolf (Ed.), Methane Conversion by Oxidative Processes Fundamental and Engineering Aspects, Van Nostrand Reinhold, 1992, 62 pp..

[17] J.G. McCarty, in: E.E. Wolf (Ed.), Methane Conversion by Oxidative Processes Fundamental and Engineering Aspects, Van Nostrand Reinhold, 1992, 320 pp..

[18] K. Van der Wiele, J.W.M.H. Geerts, J.M.N. van Kasteren, in: E.E. Wolf (Ed.), Methane Conversion by Oxidative Processes Fundamental and Engineering Aspects, Van Nostrand Reinhold, 1992, 259 pp..

[19] C.A. Mims, R. Mauti, A.M. Dean, K.D. Rose, J. Phys. Chem. 98 (1994) 13357.

[20] Y.S. Su, J.K. Ying, W.H. Green, J. Catal. 218 (2003) 321.

[21] P.M. Couwenberg, Q. Chen, G.B. Marin, Ind. Eng. Chem. Res. 35 (1996) 3999.

[22] D. Wolf, M. Slinko, M. Baerns, E. Kurkina, Appl. Catal. A 166 (1998) 47.

[23] G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, SH. Song, W.C. Gardiner Jr., V.V. Lissianski, ZW. Qin, http://www.me.berkeley.edu/gri_mech/.

[24] P. Barbé, F. Battin-Leclerc, G.M. Côme, J. Chim. Phys. 92 (1995) 1666 http://www.ensic.inpl-nancy.fr/DCPR/Anglais/GCR/generatedmecanisms/.

[25] K.J. Hughes, T. Turanyi, M.J. Pilling, http://www.chem.leeds.ac.uk/Combustion/Combustion.html.

[26] M.V. Petrova, F.A. Williams, Combust. Flame 144 (2006) 526.

[27] H. Wang, M. Frenklach, Combust. Flame 110 (1997) 173.

[28] J. Appel, H. Bockhorn, M. Frenklach, Combust. Flame 121 (2000) 122.

[29] B. Eiteneer, M. Frenklach, Int. J. Chem. Kinetic 35 (2003) 391.

[30] E.S. Oran, J.P. Boris, Numerical Simulation of Reactive Flow, 2nd ed., Cambridge University Press, Cambridge, UK, 2001.