Procedure and related tools proposed for the modeling gas-phase mechanisms involved in chemical vapor deposition: Application to CVD of SiC

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Chemical reactions occurring in the gas-phase usually play a determining role in chemical vapor deposition. Despite their importance gas phase reactions have been neglected for a long time in CVD models, and most of the chemical schemes used today in CVD reactor models are still selected on a purely empirical basis. A rigorous three-step procedure including construction, analysis and reduction of complex gas-phase mechanisms can be used to analyze reaction pathways and select a set of gas-phase reactions for CVD reactor modelling. In the present paper, the three-step procedure is presented and exemplified in the case of the Si-C-H chemical system involved in silicon carbide (SiC) deposition. The results concerning CVD of SiC are presented in the full paper. Only the method is presented in this extended abstract.

The first step of the procedure is the construction of a complex (full) chemical mechanism that is the determination of rate constants for a large set of elementary reactions involved in the chemical system. Provided that accurate thermodynamic data are available for the compounds, the main difficulty lies in the determination of the temperature and pressure dependence of the rate constants that can be either measured or estimated. Rice Ramsperger Kassel (RRK) methods, which are based on Transition State (TS) theory, are well-suited for the determination of this pressure dependence. The RRKM (RRK+Marcus) model is the most sophisticated version of RRK theory. In this model, a realistic description of the geometry and internal degrees of freedom of the TS allows the determination of the high pressure rate constant. The pressure dependence is obtained by solving a master equation for the collisional energy transfer. When TS are not available, calculations based on the simpler Quantum version of the RRK theory (QRRK) can be used to fit experimental data.

The second step of the procedure is the analysis of the stoichiometric and parametric information included in the mechanism. The stoichiometric information is related to the chemical pathways described by reactions, the parametric information depends on the value and accuracy of the thermodynamic and kinetic data that characterize elementary reactions. Several methods can be used to analyze the reaction schemes:

- the sensitivity analysis identifies the rate limiting steps
- the reaction flow analysis determines the chemical pathways
- the rate-of-reaction analysis allows the understanding of the mechanism
- the eigenvalue-eigenvector analysis identifies the characteristic timescales and directions of the chemical reactions.

Some of these methods have already been used to study CVD systems, but most of the analyses performed so far were based on thermodynamic and kinetic criteria.

As complex chemical systems are not tractable for full-scale modelling of the process, it is necessary to reduce the size of these systems. This third step consists in determining the reaction pathways and the related molecules that are "activated" under the investigated conditions. Various methods are available to reduce complex gaseous chemical systems. These methods commonly used in the combustion field are still almost unknown in the CVD community. These methods are usually divided into methods involving time-scale analysis and methods that do not.

Among the methods that do not involve a time-scale analysis, the Turanyi's method or "redundant species and reactions" method reduces the number of reactions and species involved in the chemical scheme. In the Turanyi's method, each species is individually tested to check if it is an important, necessary or redundant species under the selected conditions. Once deleted the negligible species, the information provided by the remaining reactions is tested, and those which are found negligible (i.e. reactions not involved in important pathways, and the rate constant of which does not influence the concentrations of species) are suppressed from the mechanism. The main advantage of this method is that a significant reduction of the number of species and reactions may be obtained. Furthermore, the reduced chemical system is chemically equivalent to the initial one under the selected conditions, and reveals the chemical pathways that are developed. Conversely, the main drawback of the method is that a preliminary analysis of the gas phase is required to determine the important species. It is also a time-consuming approach as each species requires a simulation for being tested, and the reduced system is only valid for the selected conditions of the reduction.

The Intrinsic Low Dimensional Manifold (ILDM) method is based on time-scale analysis. It is aimed at reducing the stiffness of the system by decoupling slow and fast processes. Local equilibrium is assumed for the fastest time-scales. This method relies on the Jacobian analysis. In contrast to other methods based on time-scale analysis, such as Computational Singular Perturbation, CSP the ILDM method does not require the knowledge of species that are either in quasi steady-state or in partial equilibrium. The sole inputs of the method are the chemical mechanism and the dimension of the manifold used to describe the reduced system in the state space. This method implies a high degree of reduction and only one calculation is necessary.