

Application of Detailed Description of Heterogeneous Reaction Kinetics to Simulation of Hydrogen Ignition and Oxidation in Filtration Layer of Solid Materials

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Introduction

Autothermal oxidation of various compounds (light hydrocarbons, biogas, various technological flammable gases, etc.) in filtration reactors ("inert" solid porous medium) is a promising way to efficient energy production. Filtration combustion (FC) can also be considered as an energy-saving technology, e.g. of syngas production from methane. Optimization and scaling-up of such processes require an adequate modeling that includes a detailed kinetic scheme on the level of elementary reactions and a reliable description of mass- and heat-transfer phenomena. Recently we reported [1,2] an approach to the modeling of methane transformation to syngas in a FC regime, which includes the description of gas-phase reaction network and corresponding computation procedures. However, the kinetic scheme could not be considered as a satisfactory complete one because the problem of description of surface kinetics was not solved at that stage [2]. Although we could follow the approach often used in gas phase kinetics and add the kinetic scheme with the steps of the type



such approach would destroy the whole logic of the modeling and also leads to substantial mathematical problem due to the impossibility to write correctly mass-balance equations.

In the present work we applied to the problem of FC modeling an approach previously developed to describe a heterogeneous-homogeneous catalytic oxidation of methane and other light hydrocarbons [3,4]. Hydrogen oxidation was chosen as a model reaction because of several reasons. Being a representative example of branched chain reaction, hydrogen oxidation can be adequately described by a relatively small set of elementary reactions with reliable kinetic parameters. The kinetic scheme that describes hydrogen oxidation operates with the same types of particles and elementary reactions as those, present in the schemes applicable to oxidation of much more complex compounds (e.g. hydrocarbons and their derivatives). Moreover, all reaction steps used to describe hydrogen oxidation are also present in the schemes of oxidation of any organic compound. In other words, the results obtained in simulations of hydrogen oxidation can be applied and further developed to simulate more complex oxidation processes.

Description of the Model and Results of Simulations.

Overall, the kinetic scheme was compiled according to the principles formulated in [4]. Gas-phase part of the scheme was represented by 40 elementary reactions (20 reversible

reactions in forward and backward directions) of molecules (H_2 , O_2 , H_2O_2 and H_2O), atoms (H and O), and radicals (OH and HO_2). Most of their kinetic parameters were taken from reliable reviews and databases; those absent in the mentioned sources were evaluated as described in [4].

According to the approach suggested in [3,4], the reactivity (stoichiometry of elementary reactions and their kinetic parameters) of surface oxygen-containing sites can be described based on the following main principles:

- surface sites participating in the process can exist in three main forms - oxidized $[\text{O}]_s$, reduced hydroxylated $[\text{OH}]_s$, and in the form of oxygen vacancy $[\]_s$;
- all three main forms of surface sites participate in three main types of elementary reactions analogous to those taking place in the gas phase - H-atom transfer (e.g. $[\text{O}]_s + \text{RH} \rightarrow [\text{O}]_s + \text{R}$), O-atom transfer (e.g. $[\text{O}]_s + \text{H} \rightarrow [\]_s + \text{OH}$) and recombination/capture (e.g. $[\text{O}]_s + \text{H} \rightarrow [\text{OH}]_s$); all these reactions can proceed in both forward and backward directions;
- kinetic parameters of these elementary reactions follow the same regularities as those of the same type taking place in the gas phase.

The detailed procedure of the evaluation of kinetic parameters for heterogeneous reactions based on the collision theory and experimental thermochemical data for surface sites is described elsewhere [3,4]. In this work, the parameters evaluated in the cited papers for a model Li/MgO catalyst were taken as a useful example.

It was assumed that reaction in a stoichiometric mixture of hydrogen and oxygen (1 : 0.5 in 10-fold volume excess of inert gas) begins at 830 K and 1 atm. Both in a free gas phase and in the presence of solid particles the system is considered as spatially uniform, i.e. all surface sites are equally accessible for gas particles with no diffusion constraints. The number of heterogeneous sites was calculated assuming that free gas space in the reactor is filled with solid oxide particles of sphere shape and ~5 mm diameter ($1.47 \times 10^{-8} \text{ mol cm}^{-3}$).

Both isothermal and adiabatic regimes of H_2 - O_2 reaction were simulated. Despite obvious differences of results obtained in these two regimes, the main conclusions about the role of surface reactions are independent on thermal effects. In order to demonstrate that in the phenomena under discussion kinetic factors play a primary role, we present here the simulated data for isothermal regime. A typical example of the development of the process in homogeneous and surface-affected regimes is presented in Fig.1. From the upper part of the Figure it is clear that in the case of the reaction in a free gas space, after an induction period of about 10^{-2} s. a kinetic ignition is taking place. Unlike that, in the presence of surface sites the process becomes "smooth" and proceeds without ignition, although the initial rate in this case is higher than in homogeneous reaction. At increasing concentration of surface sites, heterogeneous initiation becomes more important and the process progressively shifts from a classical ignition-type to a linear one characteristic for catalytic reactions.

The bottom part of Fig.1 shows that these visible changes in the reaction kinetics are due to a dramatic shift in the composition of intermediate products. Indeed, whereas in the case of homogeneous reaction the major intermediate particles are active H, O and OH, surface reactions rapidly transform them into inactive HO_2 radicals and hydrogen peroxide - relatively stable intermediate molecular product (H and H_2O_2 are shown in Fig.1 for illustration). Since the above mentioned active particles (H, O and OH) are those responsible for chain branching during hydrogen oxidation [2], the character of the surface-assisted process shifts to linear chain with a very limited contribution of branching at the expense of hydrogen peroxide dissociation.

Conclusions.

The accounting of realistic elementary heterogeneous reactions and their kinetic parameters allows one to reproduce in simulations a well-known effect of heterogeneous extinguishing the ignition in hydrogen-oxygen mixtures without any artificial assumptions, such as "wall" reactions (1) of radicals. Instead, very rapid heterogeneous reactions of chain transfer lead to a qualitative shift in the composition of intermediate species in the gas phase and prevent chain branching with a participation of active H, O and OH particles.

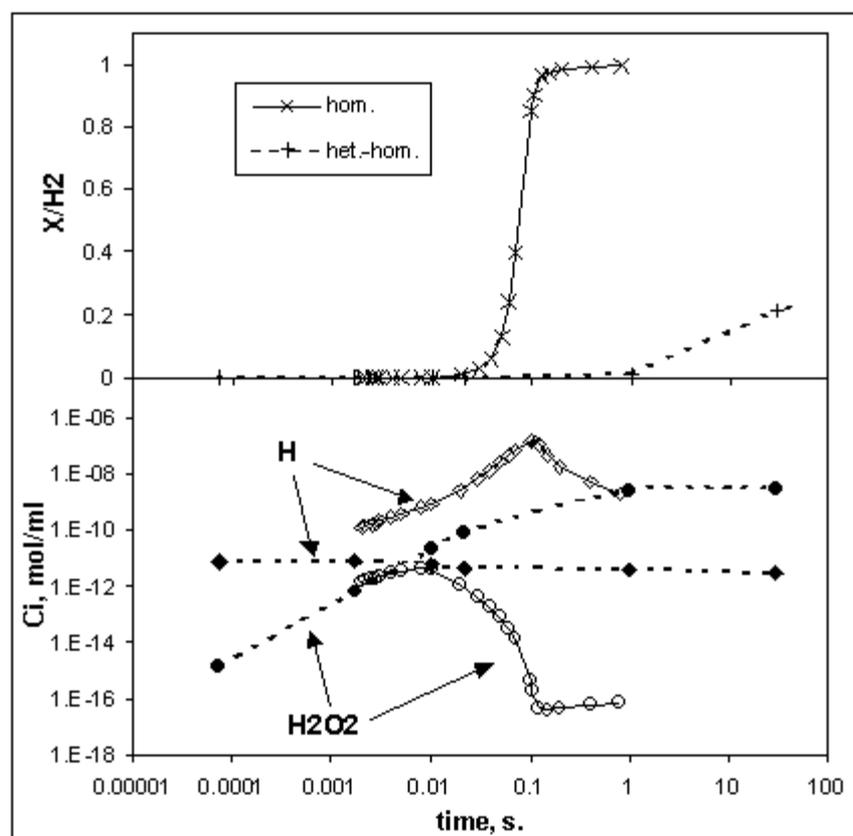


Fig. 1. Simulated data on hydrogen conversion (X/H_2) and concentrations of selected species (H-atoms and H_2O_2 molecules) vs. time in stoichiometric H_2-O_2 mixture at 830 K and 1 atm.; homogeneous gas reaction - solid lines, heterogeneous-homogeneous reaction - dashed lines.

References.

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