A combined quantum chemistry and computational fluid dynamics study of silicon dioxide and NO_x production in exhaust gas from silicon furnaces

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Silicon is produced on an industrial scale by heating quartz with coal, coke, or wood in a furnace. The gas released from the process consists of large amounts of CO, with smaller amounts of H_2O, SiO and other species. This gas is burnt in the furnace hood where it meets an inflow of air. The resulting exhaust gas consists of, e.g., CO_2, SiO_2 particles (silica dust), and NO_x. Emissions of the latter two species have been found to be strongly correlated. Numerical modeling of the combustion process, including gas flow and chemistry, is an attractive way of understanding this correlation and to design measures to reduce emissions, especially NO_x.

Unfortunately, there is a complete lack of reliable experimental rate data on the gas phase formation of SiO_2, i.e., reactions of SiO with O_2, OH, and other oxygen-bearing species. In an effort to rectify this, we have aimed to obtain estimates of the rate constants in the relevant temperature range of the most important SiO_2 forming reactions using DFT and CCSD(T) calculations coupled to Transition State Theory rate calculations. To assess the quality of the calculated rate constants, we have also studied the analogous reactions of CO leading to CO_2. Agreement with available experiments is good and the calculated rate constants are thus considered to be reliable. These are included in the reaction scheme together with tabulated rate constants for other important gas phase reactions.

Computational Fluid Dynamics, CFD, is used to model the combustion process, i.e., flow, heat transfer, and thermochemistry in 3D space. Conservative transport equations for mass, momentum, and energy are discretized unto a computational mesh describing the geometry. Since the flow is highly turbulent, a time averaging procedure of the relevant equations is used and turbulent mixing effects are taken into account by turbulence modeling (k - ε - standard model). The equations are coupled with a chemistry solver to account for formation and destruction of species due to chemical reactions. For combustion, the Eddy Dissipation Concept, EDC, is used where the reaction rate becomes a function of turbulent mixing and Arrhenius expressions. A steady-state solution with thermodynamic and chemical equilibrium is found. The CFD simulations have been performed with and without the SiO_2 forming reactions included.

The results indicate that the formation of NO_x and SiO_2 particles cannot be treated separately. Rather, the reactions responsible for SiO_2 formation also drive the NO_x formation, e.g., through the release of O atoms and heat release in secondary reactions with H_2O and CO. This gives an order of magnitude larger NO_x production rate than in the case without SiO_2 formation included, in very good agreement with measurements on the industrial setup. This is the first time the correlation between NO_x and SiO_2 dust formation has been quantified using simulations.