論文題目 　 Wall chemical effect on low temperature oxidation in weak flame
　　　　　　 (Weak flame の低温酸化反応における壁面の化学的効果)

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The economic, social and cultural development of our entire human society is highly depended upon a consistent supply of energy, and combustion technology is and will still be the backbone of energy conversion processes. More fundamental understanding of the underlying sub-processes and their mutual interaction in the complex combustion system is indeed needed. Flame-wall interaction (FWI) is one specific problem that demands our great attention. Wall surface acts as both a heat sink and a surface reaction site for species, which may quench the flame due to the decreased flame temperature and the reduced numbers of active intermediates. Previously studies with the methane normal flame suggested that the wall chemical effect only exert influence on the flame with high wall temperature (> 1000 K), while wall thermal effect is dominant for low temperature wall. Since for most of the applications, e.g. engine, the wall temperature is hard to reach 1000 K, wall chemical effect has been considered as negligible for many studies.

However, the above conclusion is only given for the high-temperature oxidation. The wall chemical effect on the low-temperature oxidation has not been investigated before. The low-temperature oxidation is the process that prepared the radical pool for the thermal ignition, thus it has a significant influence on ignition control, engine knocking control and emission reduction. Investigation of the wall chemical effect on low-temperature oxidation provided an important opportunity to advance our knowledge of the flame-wall interaction during the ignition process.
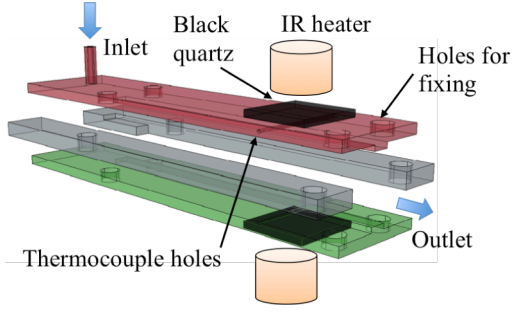
Figure 1. Scheme of the micro flow reactor.

The weak flame is chosen as the target flame, since it is a stable flame, but has the same characters as the ignition process. In this thesis, the species (DME, CO, CO_2, HCHO and OH) distributions of the weak flame in the channel with different wall materials have been measured with gas chromatography (GC) and planar laser-induced fluoresces (PLIF) system. Numerical simulations with detailed gas-phase and surface reactions have been conducted to compare with the experimental data. New surface reaction model has been proposed to reproduce the phenomenon observed in experiments.

This work begins by the development of a detachable rectangular micro flow reactor with a streamwise temperature gradient. Instead of using a circular tube as in previous studies, a rectangular quartz channel with a detachable wall, shown in Fig. 1, is used for better optical access and for the thin film deposition on the channel inner surface. The flame response to the mean inlet flow velocity is examined in this rectangular channel. It found that same flame patterns are observed with the similar flow velocity range in the present rectangular micro channel as those found in the previous study using a circular tube: normal steady flames were observed in the high-velocity region (28-50 cm/s); FREI, flames with periodic ignition and extinction, were observed in the intermediate velocity region (4-28 cm/s); weak flames were observed at the flow velocity lower than 4 cm/s. The HCHO- and OH-PLIF images show weak flame, flame with spatially separated low- and high-temperature oxidation zones, is well established in the rectangular channel developed for this work.

The radical quenching phenomenon, which has reported for the normal flames, has been examined for the weak flame. Alumina or SUS321 film has been coated on one channel sidewall. The OH wall
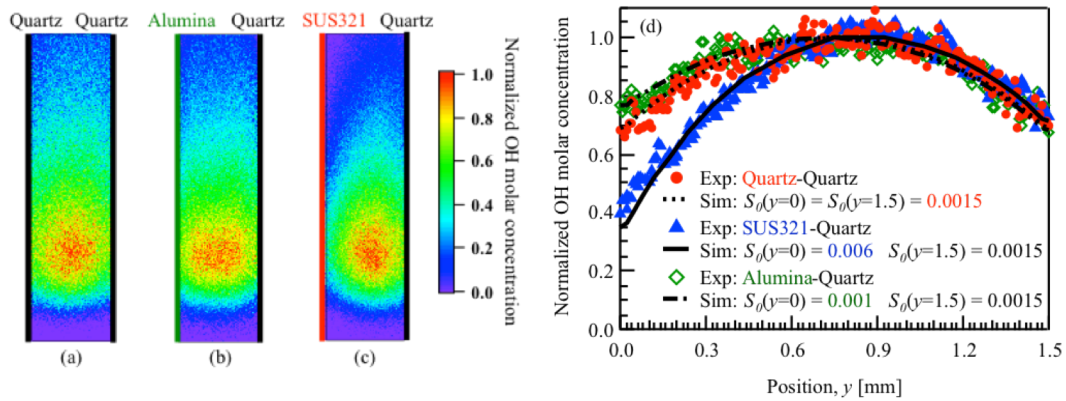

Figure 2. OH distribution in the weak flame. (a) Quartz-quartz; (b) alumina-quartz; (c) SUS321-quartz channel; (d) OH profiles in wall normal direction at the position where OH has maximum concentration in streamwise direction.

normal distribution, measured with OH-PLIF, in such an asymmetric channel was compared with that in the pure quartz channel. It found that the OH distribution changed from symmetric to asymmetric as the wall chemical boundary as shown in Fig. 2. The near-wall OH concentration decreased in the order of alumina, quartz and SUS321, which is same as the findings in the normal flame. Comparing the experimental data with the simulated results, the initial sticking coefficients (S_0) for alumina, quartz and SUS321 in the weak flame have been estimated as 0.001, 0.0015 and 0.006 respectively (shown in Fig. 2 (d)). Unfortunately, the value for quartz and SUS321 are much lower than the estimated value 0.01 and 0.1 in the normal flame. To explain the difference, a sensitivity analysis has been done based on the OH concentration for both weak and normal. It turns out that the OH concentration is most sensitive to the direct adsorption of OH in weak flame, but more sensitive to the adsorption of H than the adsorption of OH in the normal flame, due to the differences in the OH and H diffusion speeds. Therefore, the disagreement between the estimated S_0 in weak and normal flame is probably caused by the assumption of equal weight on the radical adsorptions, more specifically the equal S_0 for all species for a certain material.

Quartz has been identified as more close to inert material for radical quenching in the weak flame. SiC and SUS321 have been identified as active to radical quenching in previous work. Thus these three materials have been chosen as the typical materials for illustrate the wall chemical effect on species streamwise distributions in weak flame. SiC and SUS321 are coated as thin films on the both sidewalls of the quartz channel. DME is measured by the gas chromatography-mass spectrometer (GC-MS), while CO and CO2 are measured by the GC with thermal conductivity detector (TCD). Figure 3 shows that no significant species distribution difference has been found between the quartz and the SiC-coated channel, but very unique distributions are observed in the SUS321-coated channel, despite that SiC and SUS321 are both active for radical quenching but quartz is inert. Comparing with that in the quartz and SiC-coated channel, in the SUS321-coated channel, DME has a much higher concentration in the negative temperature coefficient (NTC) region, where CO has a lower concentration, and the maximum concentration positions of CO and CO2 are shifted to the higher temperature region. Further two-dimensional HCHO and OH species distributions in the
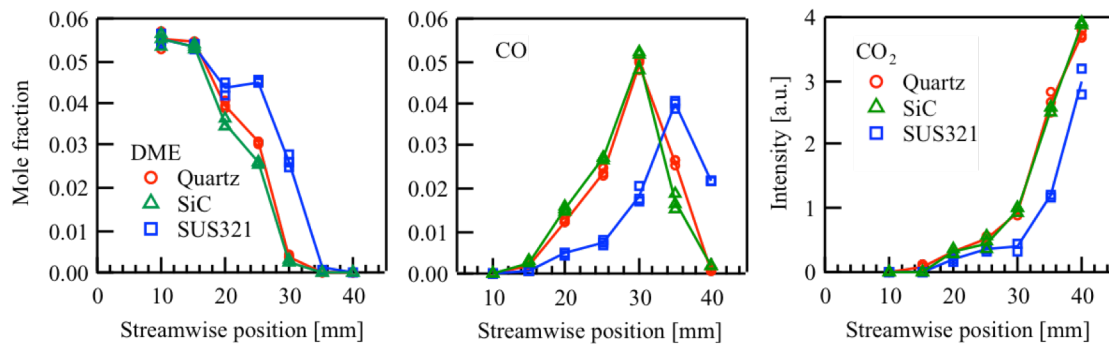

Figure 3. DME, CO and CO$_2$ streamwise profiles in weak flame.

quartz and the SUS321-coated channel are visualized by the PLIF measurement, as shown in Fig. 4. It found that in the SUS321-coated channel, the maximum HCHO concentration is becoming half of that in the quartz channel, but the HCHO zone is extended to the higher temperature region as DME. The OH in the SUS321-coated channel has a slightly higher maximum concentration than that in quartz channel, but the peak position is shifted to downstream. The results above suggested that surface reaction over SUS321 has strong influence on the low-temperature oxidation zone, leading to a higher DME concentration. As a consequence, low-temperature oxidation intermediates as HCHO are extended to the higher temperature region, which further results to a hot flame ignition delay.

Numerical simulations with detailed gas-phase and surface reactions haven been conducted with both FLUENT and DETCHEM to compare with the experimental phenomenon. Firstly, radical quenching model is attempted to describe the wall chemical effect on the species streamwise distribution in the SUS321-coated channel. However, even with $S_0 = 1$ for all radicals, the radical quenching model failed to reproduce the experimental data. Since SUS321 has around 10% Ni, the surface reaction of Ni is adopted as a base for developing the new model. Based on the experimental data, two hypotheses have been proposed for SUS321: (1) HCHO adsorption and (2) DME synthesis. The preliminary simulation results show that similar tendency as the experimental data can be obtained with the hypotheses.

This work provides the very first evidence that wall materials will affect both low- and high-temperature oxidation. The experimental results are remarkable, because previous studies suggested wall chemical effect is weak with wall temperature less than 1000 K, but present work shows that wall materials affect the low-temperature oxidation even when wall temperature is only 600 K. In the other words, the wall chemical effect may not be negligible in practical applications as engine, even when the operating wall temperatures are low. The surface reaction over the stainless surface may affect the low-temperature oxidation, further leading to an ignition delay for the hot flame. Some hypotheses for the surface reaction mechanism have been proposed for the SUS321 surface, but further research is needed to complete the surface reaction model.
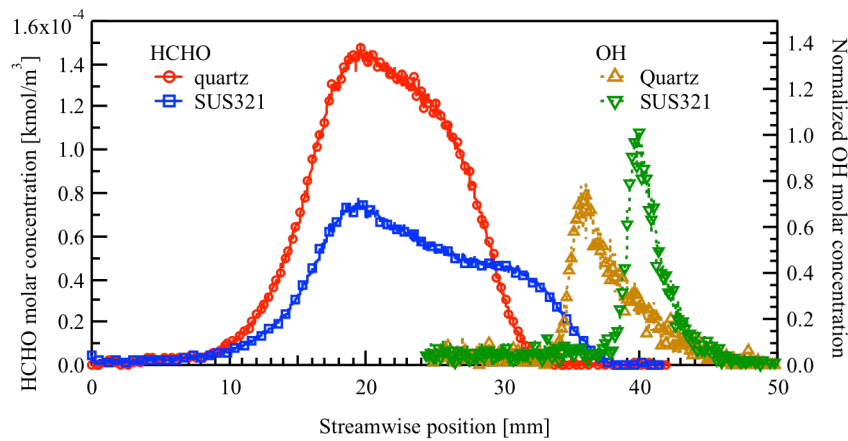

Figure 4. HCHO and OH streamwise profiles in weak flame.