Supplemental information

Formation of Polycyclic Aromatic Hydrocarbons, Benzofuran, and Dibenzofuran in Fuel-rich Oxidation of Toluene Using a Flow Reactor

Shunsuke Suzuki[a], Shota Kiuchi[b], Koichi Kinoshita[a], Yoshinaka Takeda[a], Satoshi Sakaida[b], Mitsuru Konno[b], Kotaro Tanaka[b], Mitsuharu Oguma[a]

[a]Research Institute for Energy Conversion, National Institute of Advanced Industrial Science and Technology (AIST), 1-2-1 Namiki, Tsukuba 305-8564, Japan
[b]Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

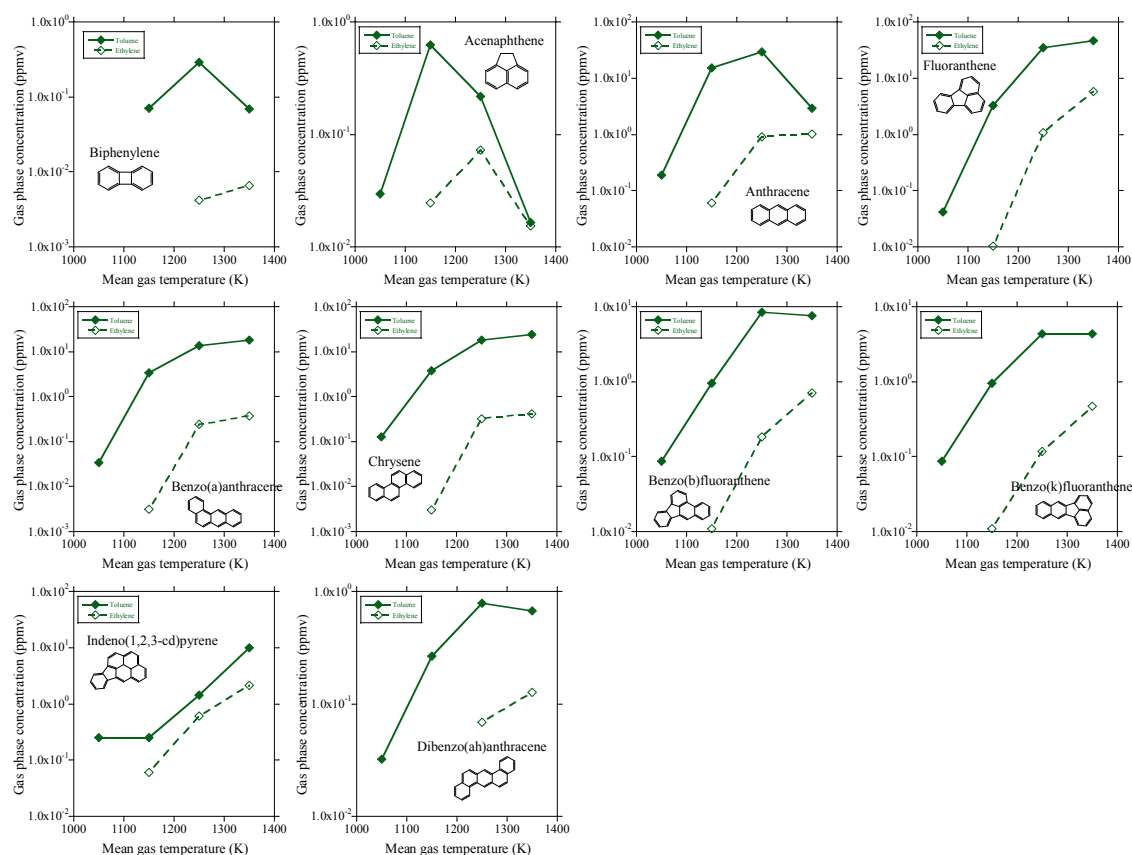# 1. Quantified PAHs other than those which are not shown in the manuscript

Figure S1. Measured mole fraction profiles of biphenylene, acenaphthene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenzo(ah)anthrancene in toluene and ethylene oxidation as functions of mean gas temperature. Experimental data of ethylene oxidation were obtained in our previous study [1]. Equivalence ratio and residence time were 9.0 and 1.2 s, respectively. Mole fractions of some PAHs in ethylene oxidation at lower temperatures were not shown because of the detection limit.
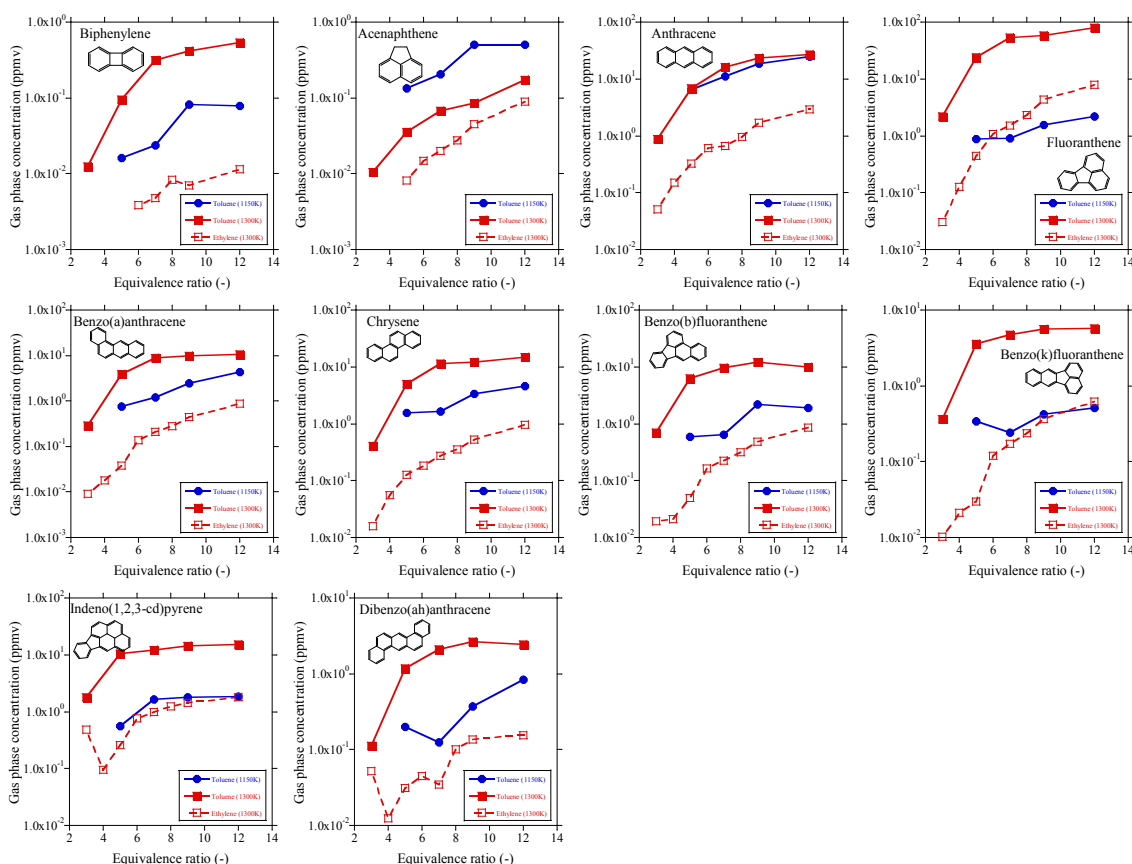
Figure S2. Measured mole fraction profiles of biphenylene, acenaphthene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenzo(ah)anthrancene in toluene and ethylene oxidation as functions of equivalence ratio at two mean gas temperatures (1150 K and 1300 K). Experimental data of ethylene oxidation were obtained in our previous study [1]. Residence time was 1.2 s. PAH concentrations in ethylene oxidation were lower than the detection limit at 1150 K.
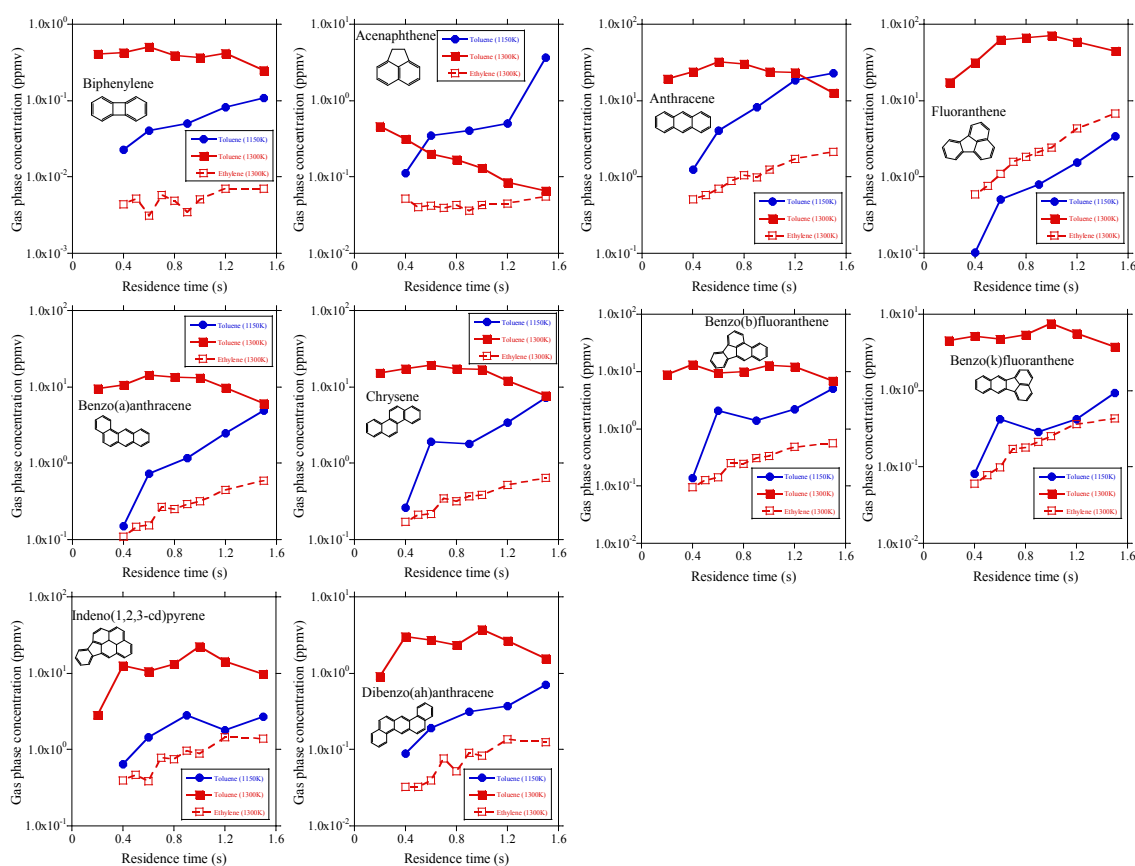
Figure S3. Measured mole fraction profiles of biphenylene, acenaphthene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenzo(ah)anthrancene in toluene and ethylene oxidation as functions of residence time at two mean gas temperatures (1150 K and 1300 K). Equivalence ratio was 9.0. Experimental data of ethylene oxidation were obtained in our previous study [1]. PAH concentrations in ethylene oxidation were lower than the detection limit at 1150 K.

## 2. Difference in important reactions for benzene and naphthalene formation

Both ROP and sensitivity analyses were conducted using the updated SJTU model to investigate the effect of the hydrocarbon structure on MAH and PAH formation. As typical MAHs and PAHs, benzene and naphthalene were adopted, respectively, and their formation pathways in both toluene and ethylene oxidation processes were explored. The reaction pathways of benzene and naphthalene in toluene and ethylene oxidation at an equivalence ratio of 9.0, residence time of 1.2 s, and gas temperature of 1250 K were studied through ROP analysis. The reaction path diagram is displayed in Figure S4. The branching ratios for producing benzene and naphthalene, estimated through ROP analysis, are shown on the arrows. When toluene was used as a hydrocarbon, benzene was primarily formed through the replacement of the methyl group in toluene with hydrogen. In other important reactions to form benzene, the hydrogen connected to the aromatic ring in toluene was abstracted and then oxidized by O_2, and then the methylcyclopentadiene radical was formed via CO elimination, followed by expansion to a six-membered ring. However, benzene was formed through the buildup of small compounds in ethylene oxidation. For instance, the propargyl radical (C_3H_3) reacted with 1,3-butadiene (C_4H_6) to form toluene, which underwent the replacement of a methyl group with hydrogen to form benzene. Another important reaction contributing to benzene formation in the ethylene/O_2/N_2 mixture was that between vinylacetylene (C_4H_4) and vinyl radical (C_2H_3).

In naphthalene formation, as depicted in Figure S4 (b), the benzyl radical ($C_6H_5CH_2$) and phenyl radical (C_6H_5) behaved as precursors in both oxidation reactions. In the case of toluene oxidation, reactions between phenyl radical + vinylacetylene and benzene + benzyne (C_6H_4) significantly contributed to naphthalene formation. Benzyne was formed through CH_3 removal from the benzyl radical. In addition, the recombination of cyclopentadienyl radicals (C_5H_5), which were produced from oxygen addition to phenyl radical followed by CO elimination, showed naphthalene formation to some extent. In the case of ethylene oxidation, hydrogen abstraction-acetylene addition (HACA) to $C_6H_5CCH_2$, which was formed through phenyl radical + acetylene followed by hydrogen addition, was the major route for naphthalene formation. The reactions correlated with methylindene ($C_9H_7CH_3$), which was obtained via HACA to benzyl radical followed by methylation of indene, contributed to some degree. As indicated in Figure S4 (a), monoaromatic compounds, such as benzene, toluene, and their derivative radicals, were easily obtained in toluene oxidation, while they had to be formed through the recombination of C2–C4 hydrocarbons in ethylene oxidation. Hence, the reaction scheme toward naphthalene formation strongly depended on the initial hydrocarbon, as well as

benzene formation.

The difference in the reaction scheme between toluene and ethylene oxidation was studied by sensitivity analysis at 1250 K to corroborate the implication obtained by ROP analysis. Figure S5 shows the sensitivity coefficients of the top five positive and negative reactions. The reactions with positive sensitivity indicate that an increase in the reaction rate enlarges the formation of benzene and naphthalene, whereas negative reactions have the opposite effect. For benzene formation, the oxidation of a radical formed via the hydrogen abstraction of toluene and the conversion reaction of toluene into benzene through the replacement of a methyl group showed large positive sensitivities in toluene oxidation, whereas hydrogen abstraction of ethylene and the reaction between vinylacetylene and vinyl radical to form benzene showed large positive sensitivities in ethylene oxidation. As for naphthalene formation, the reaction of the phenyl radical with vinylacetylene and the recombination of cyclopentadiene radicals exhibited large coefficients in toluene oxidation. In contrast, the hydrogen abstraction of ethylene still possessed the largest positive coefficients in ethylene oxidation. These results indicate that the bottlenecks for MAH and PAH formation in ethylene oxidation are ethylene reactivity and the formation of aromatic structures, while MAHs and PAHs can be produced more easily in toluene oxidation because the step to form the aromatic structure can be omitted. Consequently, MAH and PAH production in the experiments became significantly larger in toluene oxidation than in ethylene oxidation.

(a) Reaction path diagram of benzene
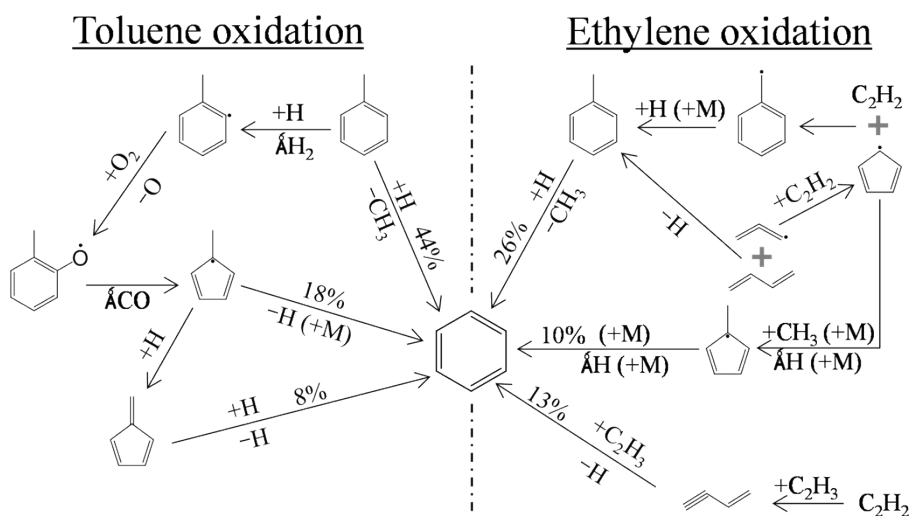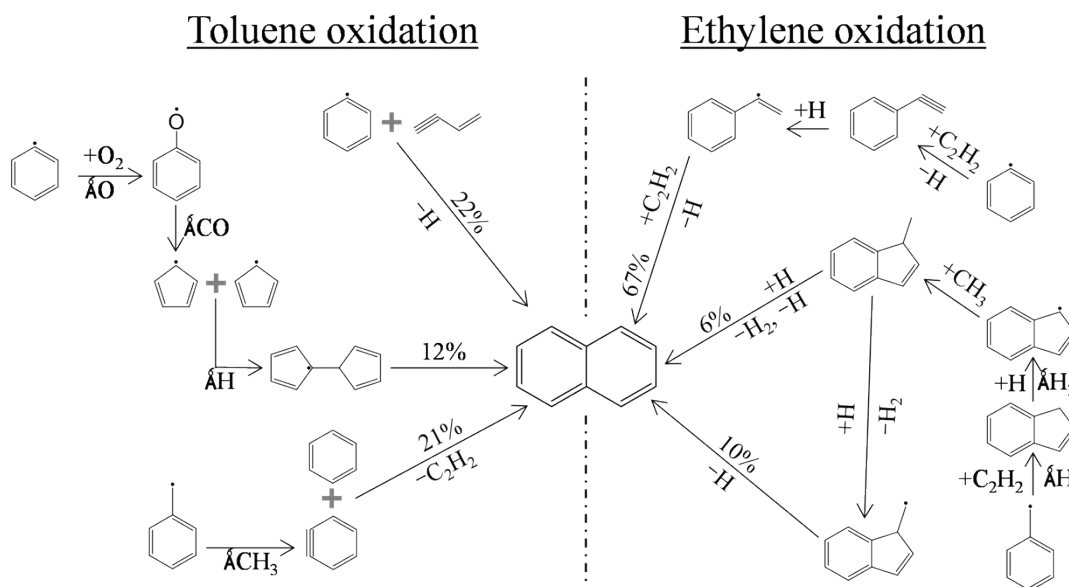
Toluene oxidation

Ethylene oxidation

Figure S4. Reaction path diagram of (a) benzene and (b) naphthalene obtained by the updated SJTU model in toluene and ethylene oxidation at an equivalence ratio of 9.0, reaction time of 0.60 s, gas temperature of 1250 K, and atmospheric pressure. Branching ratios for the formation of benzene and naphthalene estimated through ROP analysis are shown above the arrows.

Toluene oxidation Ethylene oxidation

Benzene

Toluene oxidation

$C_6H_4CH_3+O_2=OC_6H_4CH_3+O$
$C_6H_5CH_3+H=C_6H_6+CH_3$
$CH_3+C_5H_5(+M)=H+C_5H_4CH_3(+M)$
$C_6H_4CH_3=C_6H_5CH_2$
$CH_3+C_5H_5(+M)=H+C_5H_4CH_3(+M)$
$C_5H_5+O_2=C_5H_4O+OH$
$C_6H_5+CH_4=C_6H_6+CH_3$
$C_6H_6+OH=C_6H_5+H_2O$
$C_6H_6+H=C_6H_5+H_2$
$C_6H_4CH_3+O_2=C_6H_4O_2+CH_3$

-0.15 -0.10 -0.05 0.00 0.05 0.10 0.15 0.20
Sensitivity coefficient for benzene formation

Ethylene oxidation

$C_2H_4+H=C_2H_3+H_2$
$C_4H_4+C_2H_3=C_6H_6+H$
$C_6H_5CH_3+H=C_6H_6+CH_3$
$pC_3H_4+H=C_3H_3+H_2$
$CH_3+C_5H_5(+M)=H+C_5H_4CH_3(+M)$
$C_6H_6+H=C_6H_5+H_2$
$C_4H_4+H=iC_4H_3+H_2$
$2CH_3(+M)=C_2H_6(+M)$
$C_6H_5+H(+M)=C_6H_6(+M)$
$C_2H_3+O_2=HCO+CH_2O$

-0.3 -0.2 -0.1 0 0.10 0.2 0.3 0.4 0.5
Sensitivity coefficient for benzene formation

Naphthalene

Toluene oxidation

$C_6H_5+C_4H_4=Naphthalene+H$
$2C_5H_5=C_5H_5\text{-}C_5H_4+H$
$C_6H_5CH_3+H=C_6H_5CH_2+H_2$
$C_6H_5CH_2=Benzyne+CH_3$
$C_9H_7+CH_3=> C_9H_7CH_3$
$CH_3+C_5H_5(+M)=H+C_5H_4CH_3(+M)$
$C_6H_5+O_2=C_6H_4O_2+H$
$C_5H_5+O_2=C_5H_4O+OH$
$C_9H_7CH_3=>C_9H_7+CH_3$
$C_6H_5CH_3(+M)=C_6H_5CH_2+H(+M)$

-0.15 -0.10 -0.05 0.00 0.05 0.10 0.15 0.20
Sensitivity coefficient for benzene formation

Ethylene oxidation

$C_2H_4+H=C_2H_3+H_2$
$C_9H_7+CH_3=> C_9H_7CH_3$
$C_4H_4+C_4H_4=C_6H_5C_2H_3$
$C_6H_6+H=C_6H_5+H_2$
$C_5H_5+C_4H_2=C_9H_7$
$C_2H_2+C_2H_2=iC_4H_3+H$
$C_2H_3+O_2=CH_2CHO+O$
$C_9H_7CH_3=>C_9H_7+CH_3$
$C_3H_5+H(+M)=C_3H_6(+M)$
$C_2H_3+O_2=HCO+CH_2O$

-0.40 -0.20 0.00 0.20 0.40 0.60 0.80
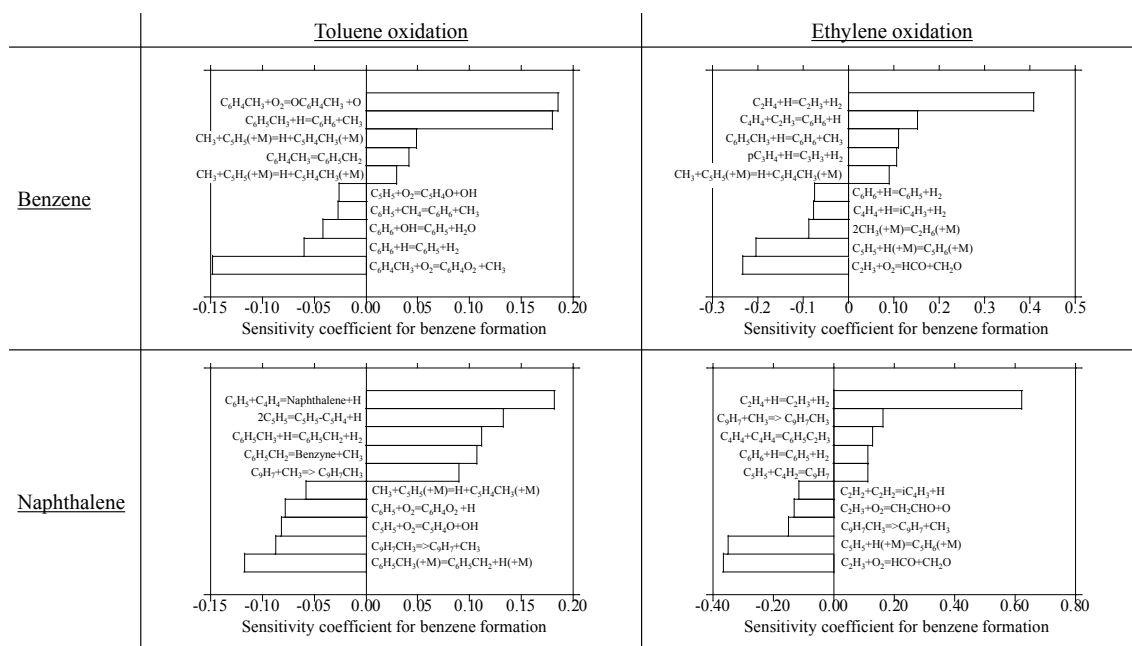Sensitivity coefficient for benzene formation

Figure S5. Sensitivity coefficient for benzene and naphthalene formation in toluene and ethylene oxidation at an equivalence ratio of 9.0, gas temperature of 1250 K, and reaction time of 0.60 s. Updated SJTU model was employed.

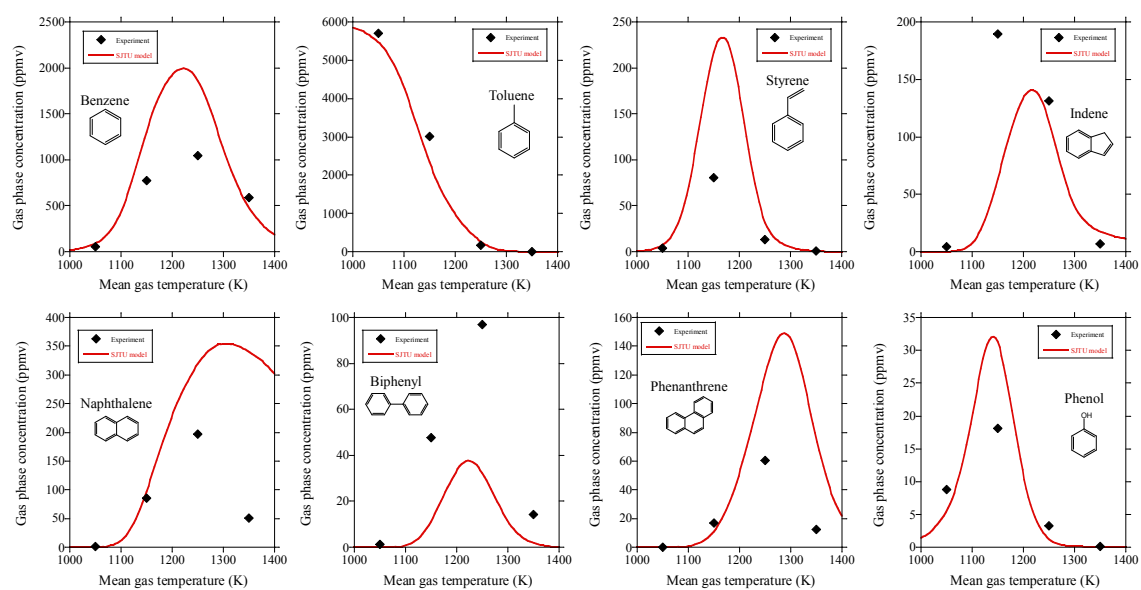## 3. Comparison of the experimental data for MAHs and PAHs with model predictions

Figure S6. Experimental and simulated mole fraction profiles of benzene, toluene, styrene, indene, naphthalene, biphenyl, phenanthrene, and phenol in toluene oxidation as functions of mean gas temperature. Solid line represents the calculated results using the SJTU model.
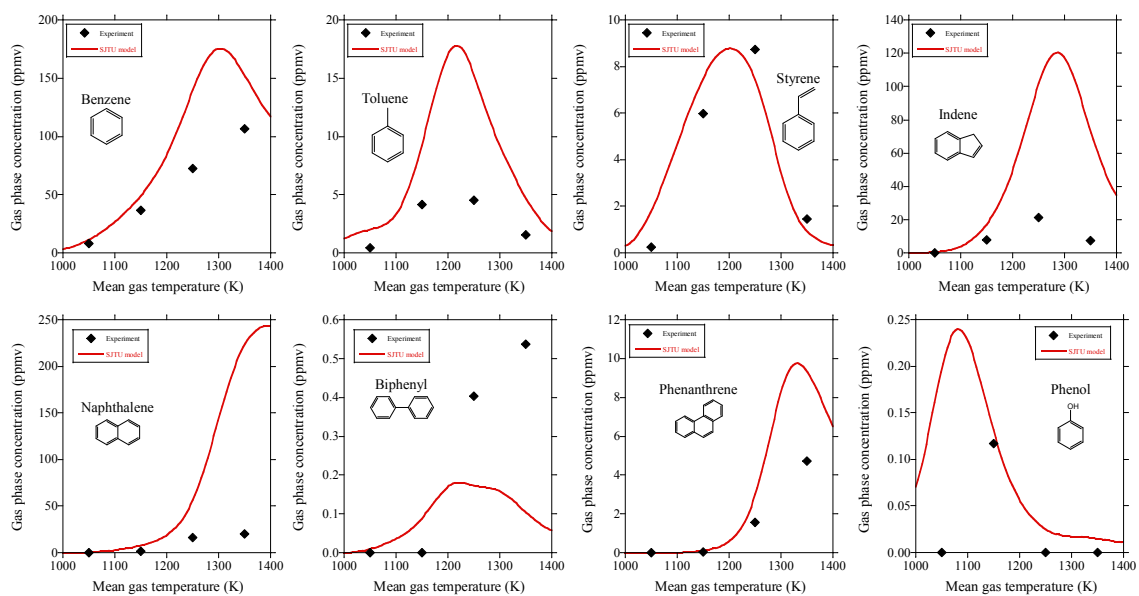
Figure S7. Experimental and simulated mole fraction profiles of benzene, toluene, styrene, indene, naphthalene, biphenyl, phenanthrene, and phenol in ethylene oxidation as functions of mean gas temperature. Solid line represents the calculated results using the SJTU model.

4. Comparison of the experimental data for benzofuran and dibenzofuran with model predictions as functions of equivalence ratio and residence time
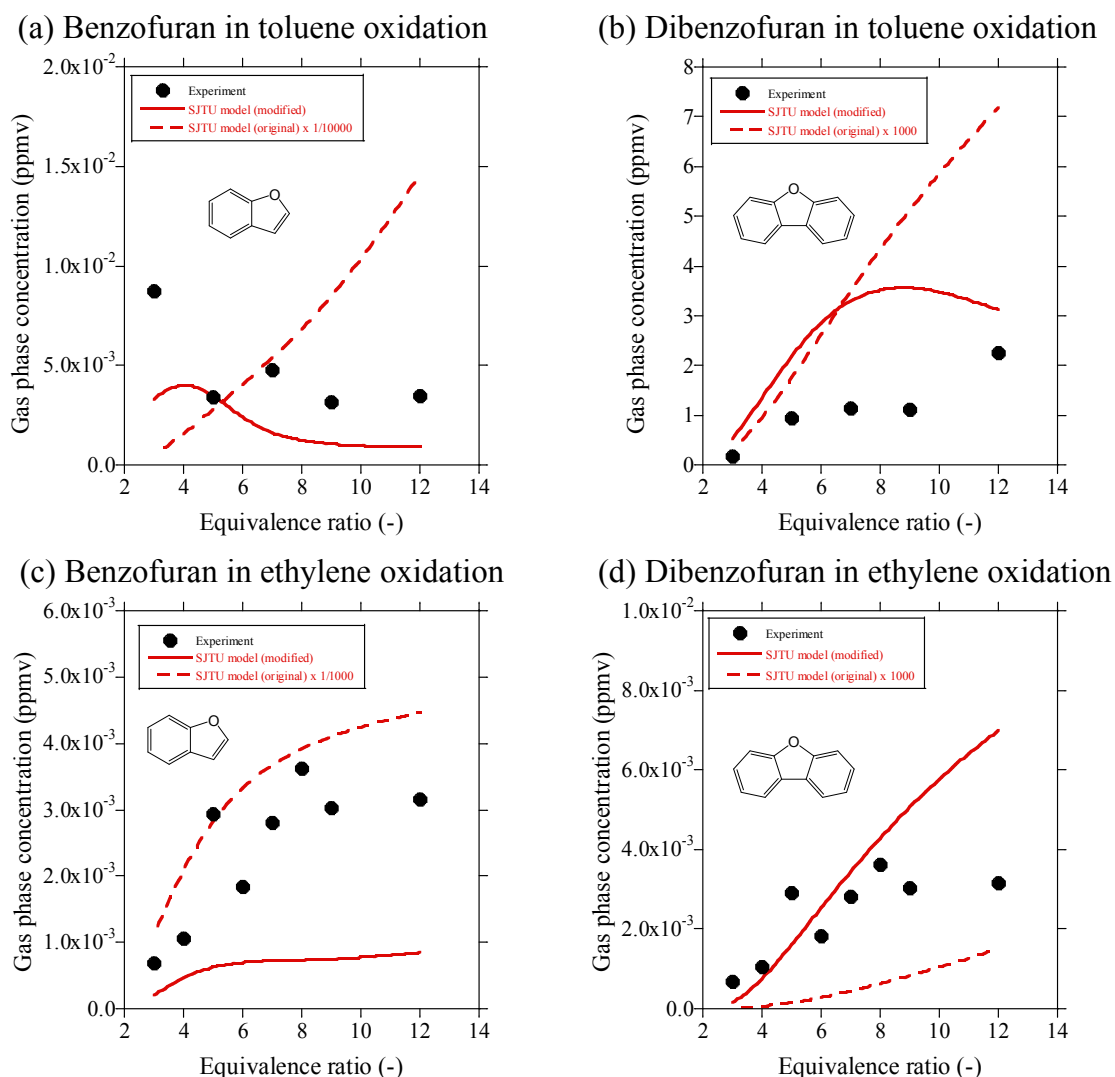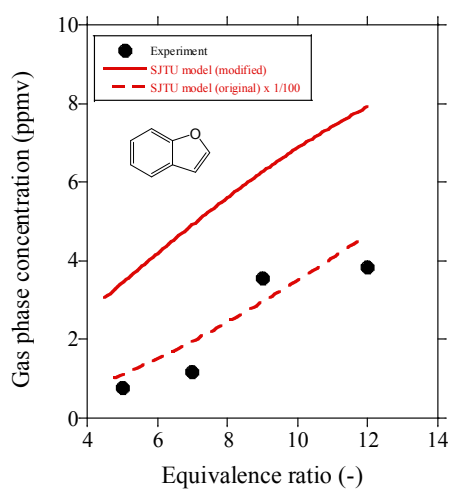
(a) Benzofuran in toluene oxidation

(b) Dibenzofuran in toluene oxidation

(c) Benzofuran in ethylene oxidation
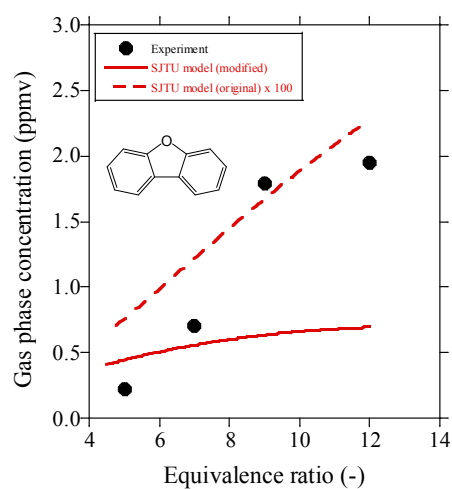
(d) Dibenzofuran in ethylene oxidation

Figure S8. Mole fraction profiles of benzofuran and dibenzofuran in toluene and ethylene oxidation as functions of equivalence ratio at a residence time of 1.2 s and mean gas temperature of 1300 K. Symbols are experimental data. Solid and dashed lines represent the simulated profiles of the modified SJTU model and the original one, respectively. Experimental data of ethylene oxidation were obtained in our previous study [1].

(a) Benzofuran in toluene oxidation

(b) Dibenzofuran in toluene oxidation
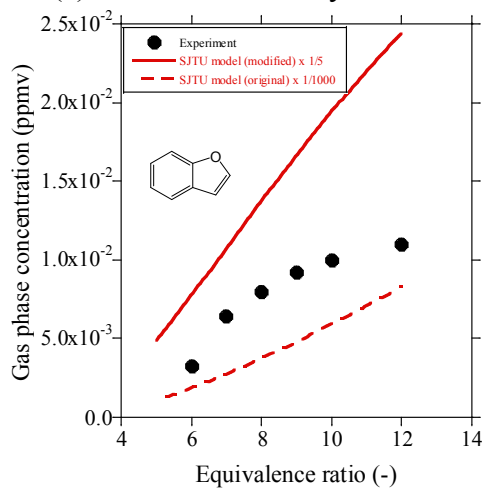
(c) Benzofuran in ethylene oxidation

Figure S9. Mole fraction profiles of benzofuran and dibenzofuran in toluene and ethylene oxidation as functions of equivalence ratio at a residence time of 1.2 s and mean gas temperature of 1150 K. Symbols are experimental data. Solid and dashed lines represent the simulated profiles of the modified SJTU model and the original one, respectively. The concentration of dibenzofuran in ethylene oxidation was lower than the detection limit. Experimental data of ethylene oxidation were obtained in our previous study [1].
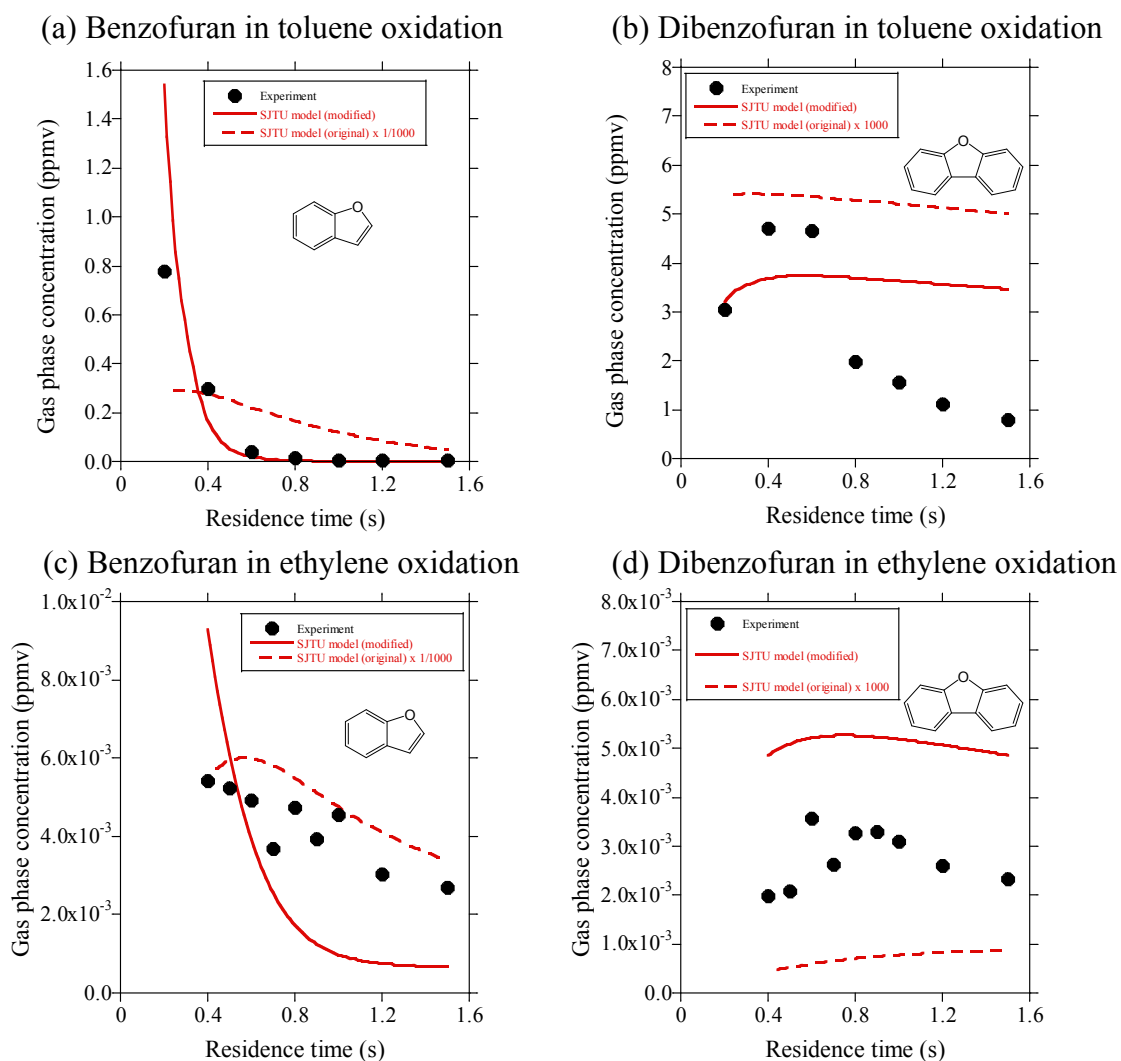
Figure S10. Mole fraction profiles of benzofuran and dibenzofuran in toluene and ethylene oxidation as functions of residence time at an equivalence ratio of 9.0 and mean gas temperature of 1300 K. Symbols are experimental data. Solid and dashed lines represent the simulated profiles of the modified SJTU model and the original one, respectively. Experimental data of ethylene oxidation were obtained in our previous study [1].

(a) Benzofuran in toluene oxidation

(b) Dibenzofuran in toluene oxidation
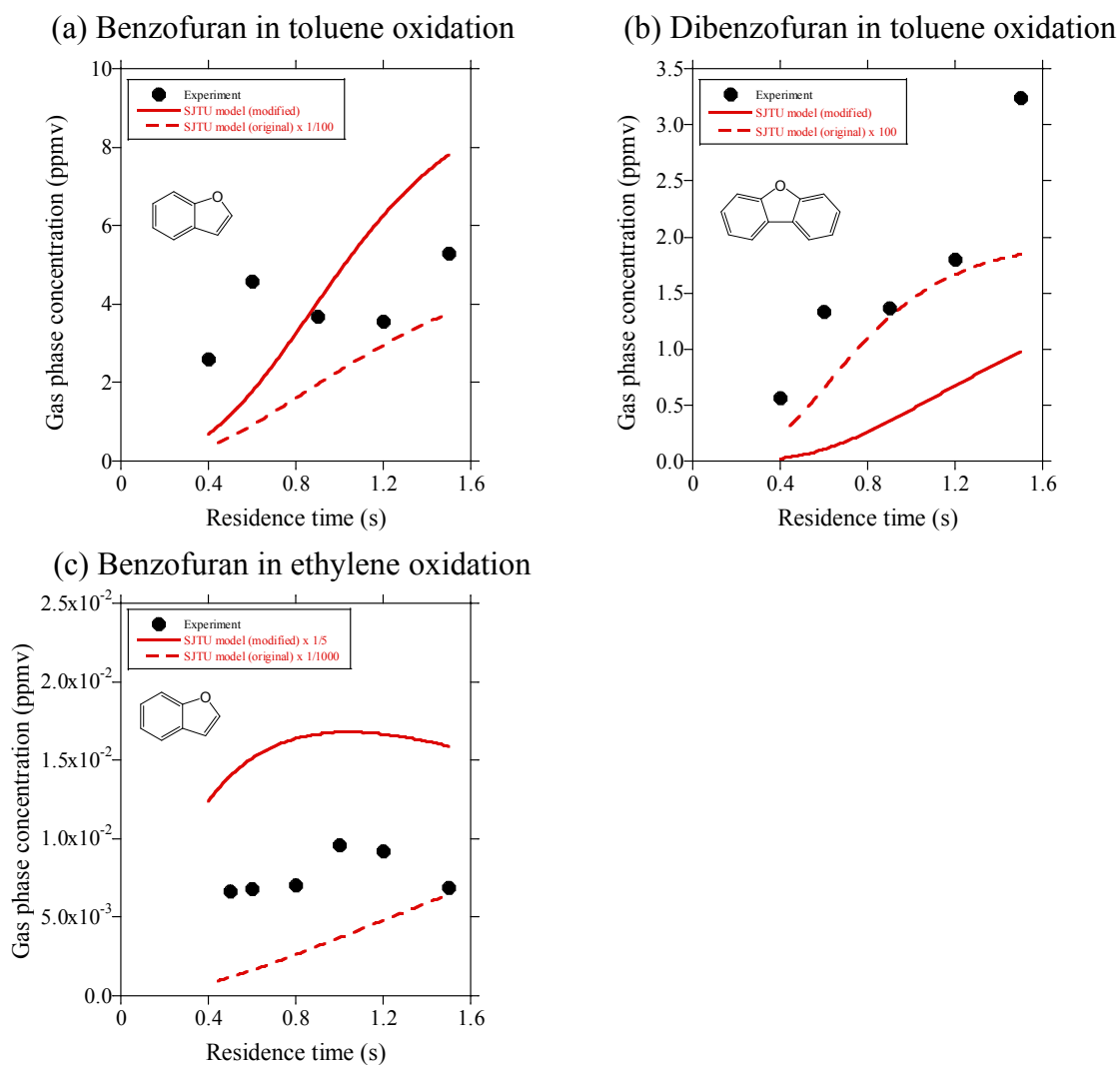
(c) Benzofuran in ethylene oxidation

Figure S11. Mole fraction profiles of benzofuran and dibenzofuran in toluene and ethylene oxidation as functions of residence time at an equivalence ratio of 9.0 and mean gas temperature of 1150 K. Symbols are experimental data. Solid and dashed lines represent the simulated profiles of the modified SJTU model and the original one, respectively. The concentration of dibenzofuran in ethylene oxidation was lower than the detection limit. Experimental data of ethylene oxidation were obtained in our previous study [1].

REFERENCES

[1] S. Suzuki, S. Kiuchi, K. Kinoshita, Y. Takeda, K. Tanaka, M. Oguma, Formation of Polycyclic Aromatic Hydrocarbons (PAHs) and Oxygenated PAHs in the Oxidation of Ethylene Using a Flow Reactor, Combust. Sci. Technol. in press (2020)