

1 **Supporting Information**

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5 **Effect of the Blocking Sites Phenomenon on the**
6 **Heterogeneous Reaction of Pyrene with N₂O₅/NO₃/NO₂**

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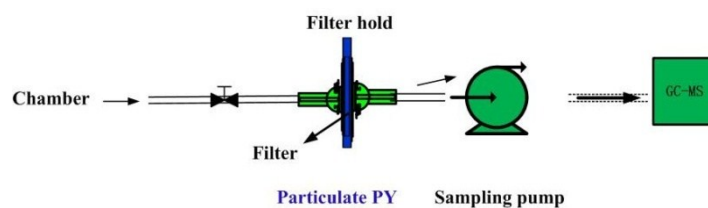
20 **1. Collecting and analyzed of products**

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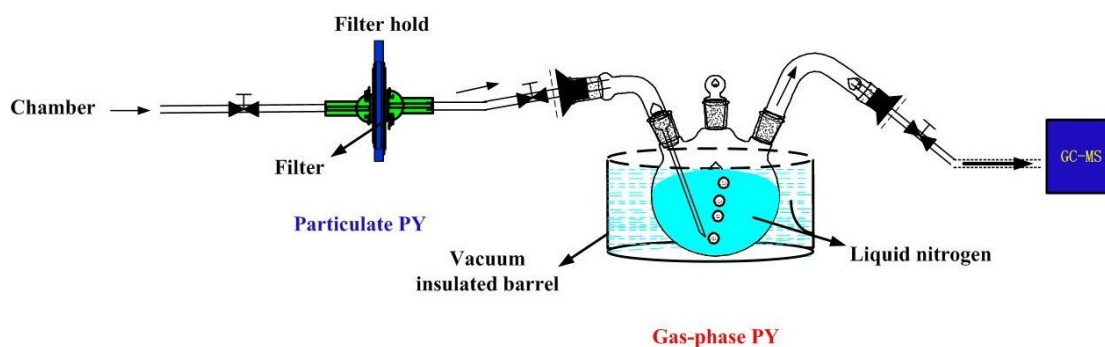
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Figure S1. The schematic diagram of collecting procedure

23 2. The partitioning ratio of PY

24 The particulate PY and gas-phase PY were microfiber filter (25 mm diameter,
 25 0.7 μm pore-size, Whatman)—liquid nitrogen washing (Figure S2). The collected PY
 26 were extracted with ~ 20 ml dichloromethane and analyzed using GC-MS. The
 27 partitioning ratio of pyrene between the gas and particle phase under our experimental
 28 condition was estimated to 0.2 be according to the relative signal intensities of gas-
 29 phase and particulate PY observed using GC-MS.

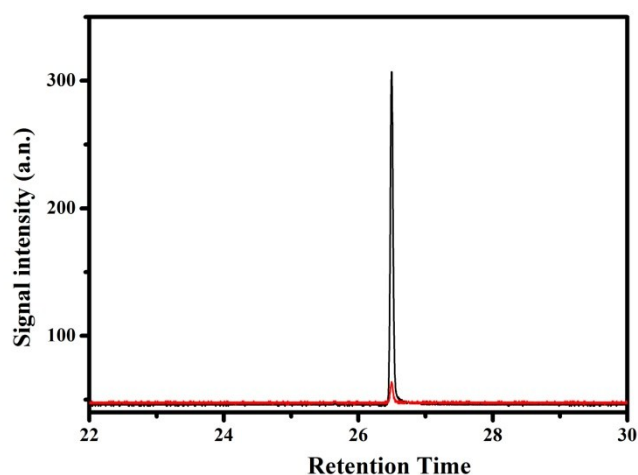
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Figure S2. The schematic diagram of collecting procedure



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34 **Figure S3.** The signal intensity of gas-phase (red line) and particulate PY (black line)

35 3. Estimation of Oxidants Concentrations

36 3.1 Estimation of initial N_2O_5 concentration

37 The amount of N_2O_5 delivered in experiments was determined by the temperature
 38 of the N_2O_5 trap (243 K in our experiments) and its vapor pressure under this
 39 temperature. The initial gas-phase N_2O_5 concentration in the chamber was calculated
 40 using the equation (2).

$$41 \quad [N_2O_5]_0 = \frac{qtT_{chamber}P_t}{V_{chamber}T_{bathe}P_0} \quad (1)$$

42 $[N_2O_5]_0$ is the initial N_2O_5 concentration, P_t and P_0 is the vapor pressure of
 43 N_2O_5 (~40 Pa) at 243 K and the standard atmospheric pressure (~101306 Pa),
 44 respectively. $V_{chamber}$ represents the volume of the reaction chamber used in our
 45 experiment, respectively. $T_{chamber}$ and T_{bathe} are the temperatures of the chamber (286
 46 K) and the cooling bath (243 K). q is the flow rate of N_2 (~0.6 L min⁻¹), t is the filling
 47 time (3~5 min).

48 3.2 Estimation of the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio in the absence of O_3

49 The NO_3 concentration in the chamber was estimated by probing the decay of
50 the isoprene. ~ 200 ppbv isoprene was added into the chamber before introducing
51 $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ mixture. The decay of isoprene was on-line monitored using VUV-
52 GTOFMS (Figure S4). The NO_3 radical concentration in the absence of O_3 are
53 calculated with the following equations (3–6).

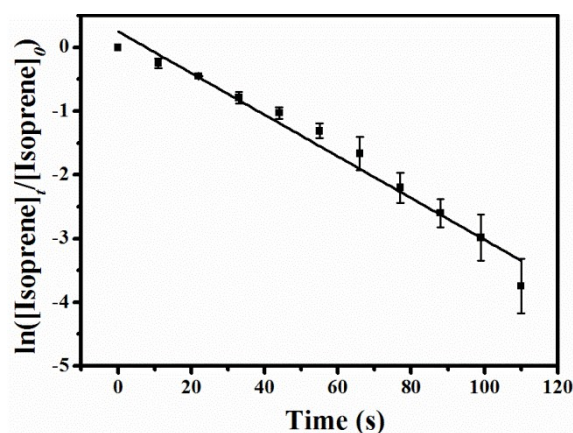


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$$-\frac{d[\text{Isoprene}]}{dt} \rightarrow k_1[\text{Isoprene}][\text{NO}_3] \quad (3)$$

56
$$\ln\left(\frac{[\text{Isoprene}]_t}{[\text{Isoprene}]_0}\right) = -k_1[\text{NO}_3]t \quad (4)$$

57
$$[\text{NO}_3] = \frac{\ln\left(\frac{[\text{Isoprene}]_t}{[\text{Isoprene}]_0}\right)}{-k_1t} \quad (5)$$

58 t is the reaction time. $([\text{Isoprene}]_t/[\text{Isoprene}]_0)$ is the loss ratio of isoprene during
59 this period. The average NO_3 radical concentrations in the reaction processes was
60 calculated to be $\sim 3.0 \times 10^{10} \text{ molecules cm}^{-3}$.



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62 Figure S4. The isoprene decay curves by exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$. The error bars

63 are obtained from three duplicate experiments.

64 Based on the obtained NO_3 level and the temperature dependent equilibrium
 65 constant K_{eq} shown in equation (7) (Sander et al., 2003), the N_2O_5 concentration was
 66 calculated to be $\sim 2.0 \times 10^{14}$ molecules cm^{-3} .

$$67 \quad K_{eq} = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2][\text{NO}_3]} = 3 \times 10^{-27} \exp(10990/T) \quad (7)$$

68 $[\text{N}_2\text{O}_5]$, $[\text{NO}_3]$, and $[\text{NO}_2]$ are the concentrations of N_2O_5 , NO_3 , and NO_2 , respectively.

69 3.3 Estimation of the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio in the presence of O_3

70 The NO_3 radical concentration in the presence of O_3 could not be estimated
 71 according to the decay of isoprene because part of isoprene was also consumed by O_3
 72 in the chamber. Although the $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ reaction was derived to
 73 NO_3 radical using O_3 , the new equilibrium in the $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ system was
 74 assumed to be established in the presence of O_3 . Both NO_3 radical and N_2O_5
 75 concentration could be calculated using the following equation:

$$76 \quad \frac{[\text{N}_2\text{O}_5]^*}{[\text{NO}_2]^*[\text{NO}_3]^*} = \frac{[\text{N}_2\text{O}_5] - k_{\text{O}_3+\text{NO}_2}[\text{O}_3][\text{NO}_2]^*}{[\text{NO}_2]^*([\text{NO}_3] + k_{\text{O}_3+\text{NO}_2}[\text{O}_3][\text{NO}_2]^*)} = K_{eq} \quad (8)$$

77 where $[\text{N}_2\text{O}_5]^*$, $[\text{NO}_3]^*$, and $[\text{NO}_2]^*$ are the concentrations of N_2O_5 , NO_3 , and NO_2 ,
 78 respectively, in the new equilibrium system. $k_{\text{O}_3+\text{NO}_2}[\text{O}_3][\text{NO}_2]^*$ is the production rate
 79 of the NO_3 radical ($k_{\text{O}_3+\text{NO}_2} = 1.4 \times 10^{-13} \exp(-2490/T)$)(Atkinson et al., 2004). Based
 80 on the iteration method, $[\text{NO}_3]^*$, $[\text{N}_2\text{O}_5]^*$, $[\text{NO}_2]^*$, the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio have been
 81 calculated and shown in Table 1.

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