Anonymous Referee #2

Zhang et al. investigated the formation of secondary organic aerosols produced from the ozonolysis of ethyl methacrylate under different experimental conditions (RH and seed aerosols). SOA were characterized using mass spectrometry and particle formation monitor using an SMPS system. Overall, the paper is very hard to follow and the discussion/interpretation weakly constrained. As a result, I recommend that the authors restructure the manuscript and provide deeper/quantitative analyses.

Answer: Thank you very much for your review and giving us valuable suggestions. The manuscript has been revised substantially according to your comments (See below).

Q1. Method parts: (1) The authors should discuss the effect of CO, how much did CO decrease the OH chemistry? Overall, you should be more quantitative when presenting the experiments and results. (2) The authors mentioned that they used a nano-DMA, which is not possible as a nano- DMA can go up to 150 nm only.

A1. (1) In this work, it could be found that about 1ppm CO was consumed for both of experiments (Figure S4). Given that the initial concentration of EM was kept to be 100 ppb prior to reaction, the high consumption of CO during the experiments may be attributed to the reaction between CO and OH radical, particle adsorption and wall-loss of chamber. Although we could not quantitate how much CO decrease the OH chemistry, two recent works from our laboratory and McFiggans et al. all indicated that higher CO levels were found to significantly change the chemical composition of SOA relative to low CO level (Zhang et al., 2020; McFiggans et al., 2019). This has been corrected in the revised manuscript (171-174).

(2) “A scanning mobility particle sizer (SMPS, TSI, Inc.), consisting of differential mobility analyzer (DMA; model 3082), condensation particle counter (CPC; model 1720), and Po210 bipolar neutralizer, was applied to measure number size distribution.” This has been corrected in the revised manuscript (145)

Q2. Please provide the number of particles as well and the evolution of the mean size. In addition, you need to provide the surface area of the particles for all the experiments. Size diameter is very different between the experiments which can play a critical role in the difference observed in the study.

A2. The number concentrations of particles have been shown in Figure 2.

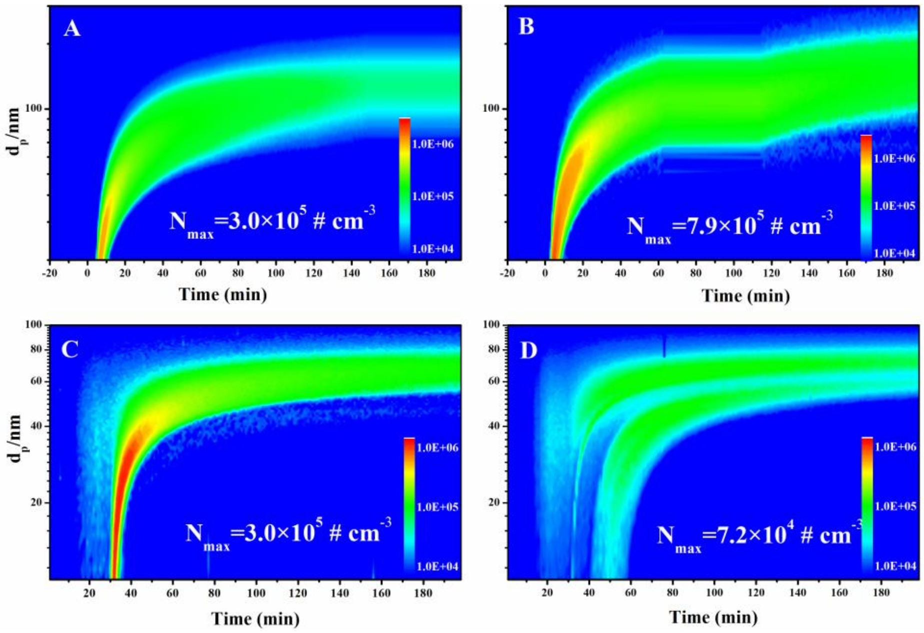

Figure 2. Size distribution of secondary aerosol as a function of time at 55 ppb SO_2 (A) and 135 ppb SO_2 (B) and under AS seed particle (C) and Acidic AAS seed particle (D).

The mean size and surface area in the SO_2 experiments and seed experiments have been shown in Figure S10 and S11. This has been corrected in the revised manuscript (235-236) and Supporting Information (Line 79-92).

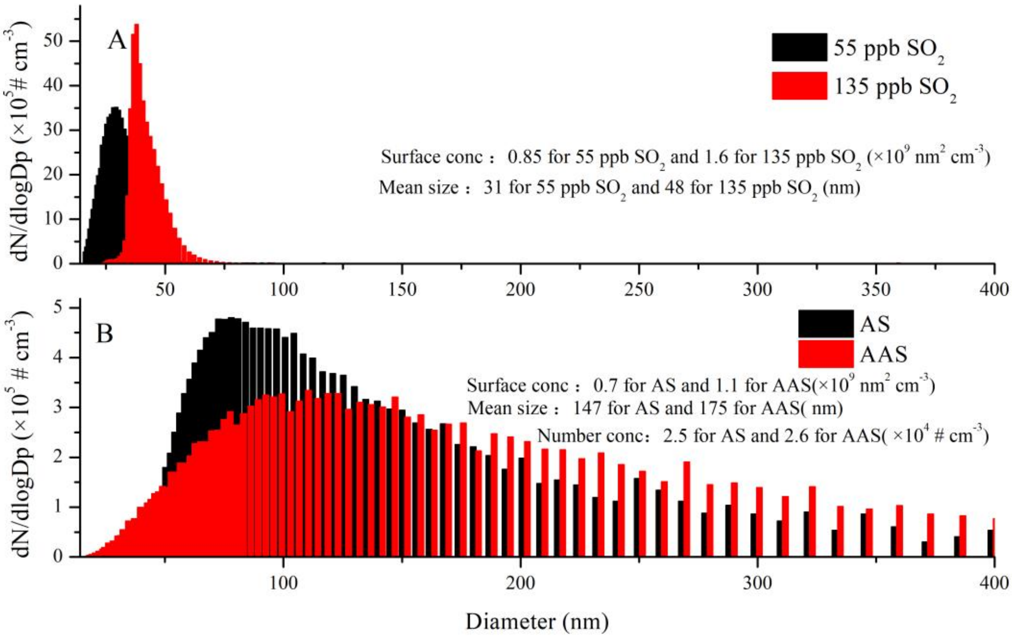

Figure S11. Number distribution of secondary particle at 55 ppb $SO_2$and 135 ppb SO_2 (A) when the number concentration was maximum; Size distribution of seed particle:

AS and AAS seed particle (B).

Q3. I would suggest also using a numbering system to discuss the experiments, it would help the reader. All experiments need to be presented in the corresponding section. The authors discuss additional experiments within the result section within providing any information.

A3. The numbering system of different experiments have been inserted in Table S1 (Line 31).

Table S1. Experimental conditions.

No.	[EM] (ppb)	[O_3] (ppb)	[SO_2] (ppb)	Seed acidity	 mass con. (μg m^{-3})	CO (ppm)	RH (%)
#1	100	200	55	-	-	38	10%
#2	100	202±4	131±3	-	-	36±1	10%
#3	100	205±6	138±6	neutral	47±5	38±1	10%
#4	100	200	138	acidity	59.3	36	10%
#5	100	205±6	135±6	neutral	42±5	38±1	45%
#6	100	200	132	acidity	52	36	45%

Results:

Q4. (1) Line 176: Why did you look at the mass of sulfate and not organics to show the SOA formation? Sulfate cannot be considered as a secondary particle –> please provide the mass of organics. (2) Please estimate the acidity for AS, AAS, and nucleated H_2SO_4 particles.

A4. (1) The Y-axis is wrong, which has been revised in Figure S6. The evolution of SOA mass has been shown in Figure S7. From AMS and SMPS data, it could be found that the increased particle acidity did not promote SOA formation during the ozonolysis of alone EM in the absence of SO_2.

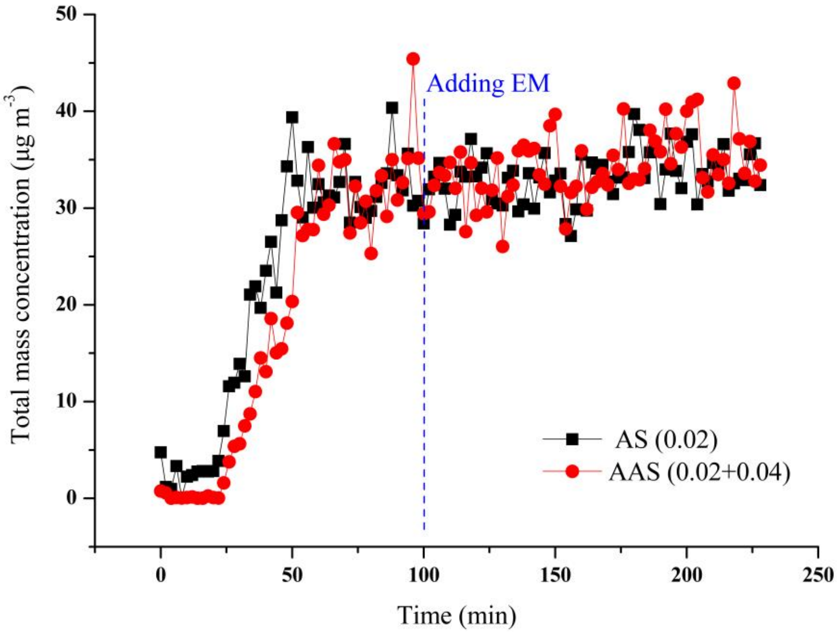

Figure S6. Evolution of secondary particles mass concentration with AS (black) and AAS (red) in the absence of SO_2 (SMPS data).

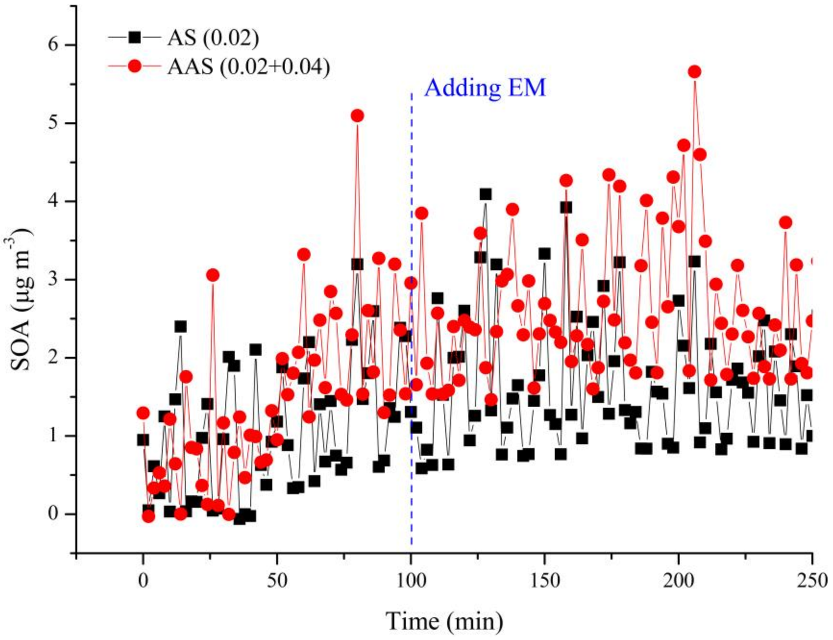

Figure S7. Evolution of SOA mass concentration with AS (black) and AAS (red) in the absence of SO_2 (AMS data).

This has been shown in the revised manuscript (Line 186-187) and Supporting Information (Line 55-62).

(2) According to the methods reported by Peng et al (2009),(Peng et al., 2019) we

estimated the pH in the particles. The acidity for nucleated H_2SO_4 particles (pH) under different SO_2 concentration have been estimated to be 3.27 and 3.46, respectively (Figure 5). The acidities for AS and AAS (pH) have been estimated to 7.3 and 4.1, respectively.

For the E-AIM model, pH was estimated as follows:

$$pH = -log_{10}(f_{(H^+)} \times X_{(H^+)})$$

Where $f_{(H^+)}$ is the activity coefficient of H^+, $X_{(H^+)}$ is the molar fraction of H^+.

This has been added in the revised manuscript (Line 370-373) and Supporting Information (Line 139-146).

Q5. Line 182: The authors should discuss aerosol surface areas before reaching such a conclusion. Provide the surface areas for the different experiments performed in this work?

A5. High SO_2 level promote the number concentration of fine particles sulfate under different SO_2 level (Figure 2A and 2B).

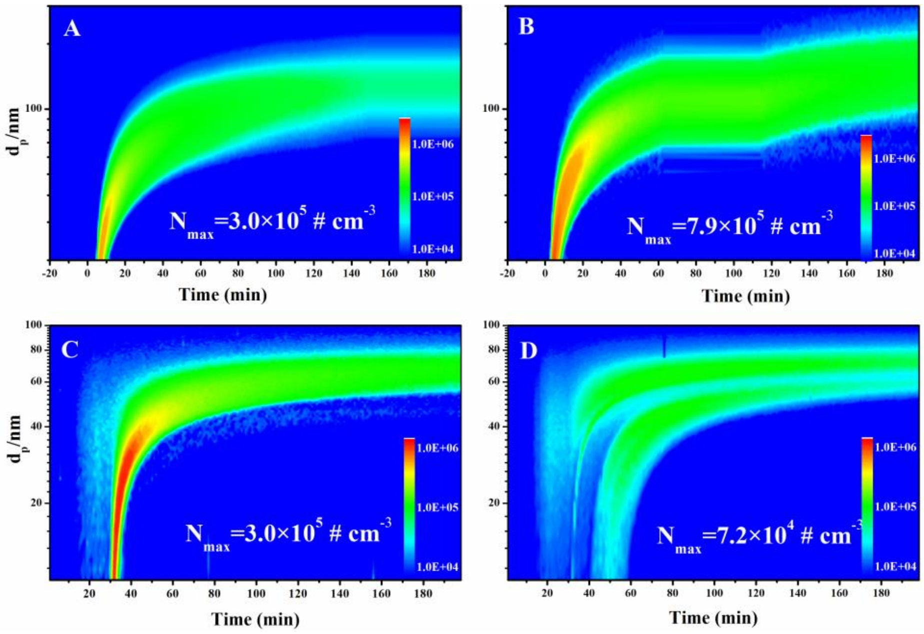

Figure 2. Size distribution of secondary aerosol as a function of time at 55 ppb SO_2 (A) and 135 ppb SO_2 (B) and under AS seed particle (C) and Acidic AAS seed particle (D).

The mean PTof size of sulfate at 135 ppb SO_2 was also higher than that at 55 ppb SO_2 (Figure S10).

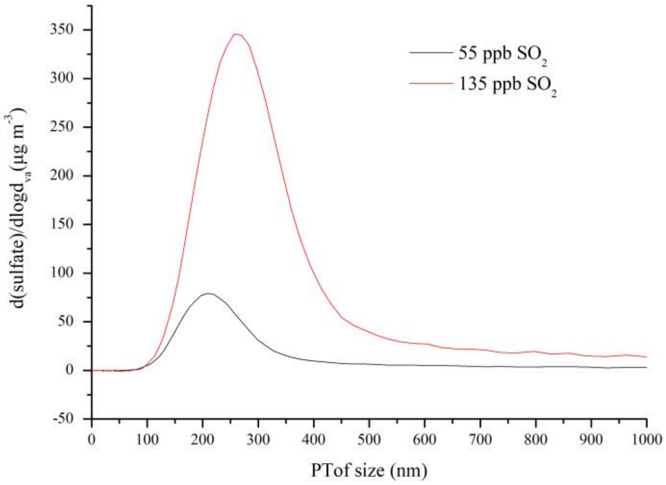

Figure S10. PTof of size of sulfate at 55 ppb $SO_2$and 135 ppb SO_2.

Moreover, the mean surface concentration and mean size at 135 SO_2 were also higher than that at 55 ppb SO_2 (Figure S11A). This indicated that high SO_2 level promoted the rapid homogeneous nucleation of H_2SO_4, which providing greater surface area and volume for the condensation of low-volatile products.

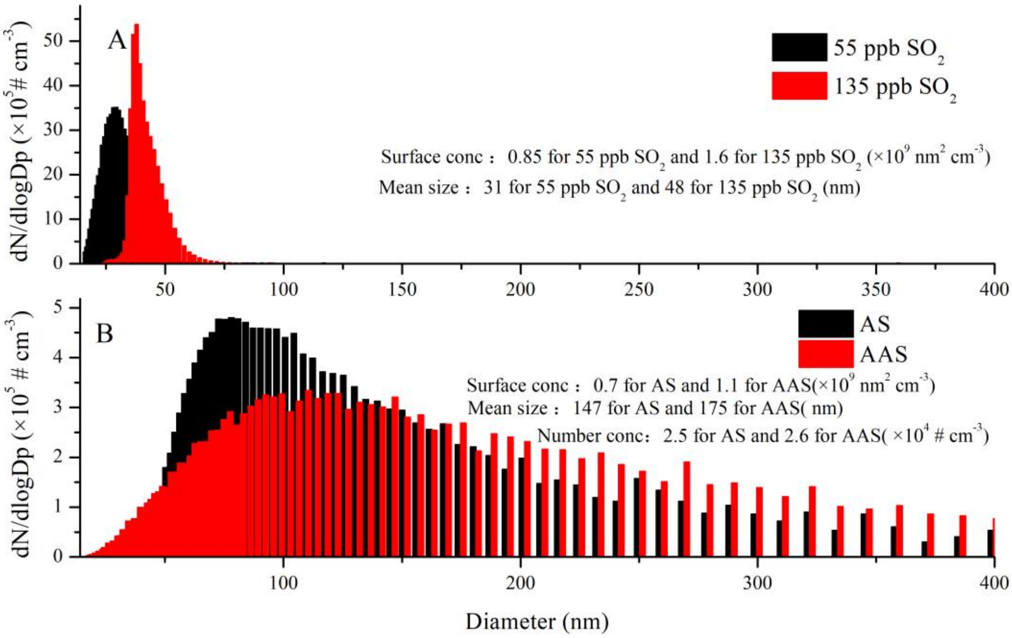

Figure S11. Number distribution of secondary particle at 55 ppb $SO_2$and 135 ppb SO_2 (A) when the number concentration was maximum; Size distribution of seed particle: AS and AAS seed particle (B).

This has been corrected in the revised manuscript (235-236) and Supporting Information (Line 79-92).

Q6. Line 184: which level/concentration?

A6. The initial concentrations of SO_2 were in the range of 132 to138 ppb in different seed experiments (Line 195).

Q7. Lines 191-192: The wording is inaccurate, SOA formation is not suppressed by reduced.

A7. This has been corrected in the revised manuscript (Line 202).

“This indicated that increased particle acidity reduced secondary particle formation in the presence of SO_2………”.

Q8. Lines 199-204: I found the impact of RH more dramatic than the impact of the aerosol acidity (i.e., reduced by a factor of 2). The authors should discuss more this aspect. I also find the conclusion of the authors poorly constrained. More details on surface area and acidity must be discussed. Indeed, condensation of H_2SO_4 will result in acidic seed particles.

A8. Yes, the change in RH indeed had an impact on the formation of EM-derived SOA and sulfate, consistent with several recent studies. SOA concentration at 45% RH was reduced by a factor of 2 relative to that at 10% RH in this work. The changes in both sulfate and SOA concentration were attributed to the competitive reaction between SO_2 and H_2O toward sCI. The suppression of H_2SO_4 concentration was attributed to the rapid consumption of sCI by water and water dimer at high RH (42%). The suppression of SOA mass loading should be ascribed to the formation of volatile organic peroxides at high RH.

The discussion on the impact of RH on SOA has been added in the revised manuscript (Line 213-220) and Supporting Information (63-78).

Q9. Lines 227-230: Are the authors suggesting that EM is oxidized by O_3 in the condensed phase and sCI react with SO_2 to form H_2SO_4 in the condensed phase? This sounds quite speculating with the data shown in this paper. in addition, if acidity aerosol promotes condensation of oxidized species, the results should show a greater formation of SOA in the presence of acidic particles. which is not the case. Later the authors mentioned that this "speculation" (line 232) is supported by some experiments. However, we have very little information on these additional experiments. For example, how experiments perform using an ATR can be used to simulate chemical reactions potentially occurring at the interface of an aerosol? The results briefly discussed in the SI are not convincing.

A9. Actually, in situ attenuated total internal reflection infrared (ATR-IR) spectra was not used to investigate the chemical reaction potentially occurring at the aerosol surface, but to investigate and compare the consumption of EM absorbed on particle surface under different condition. We first investigated the EM uptake on different using a gas mass spectrometer (QMS, GAM 200, Bremen, Germany). As shown in Figure S12, the increase in H_2SO_4 concentration indeed promoted the uptake of EM on seed particle with the increase of acidity.

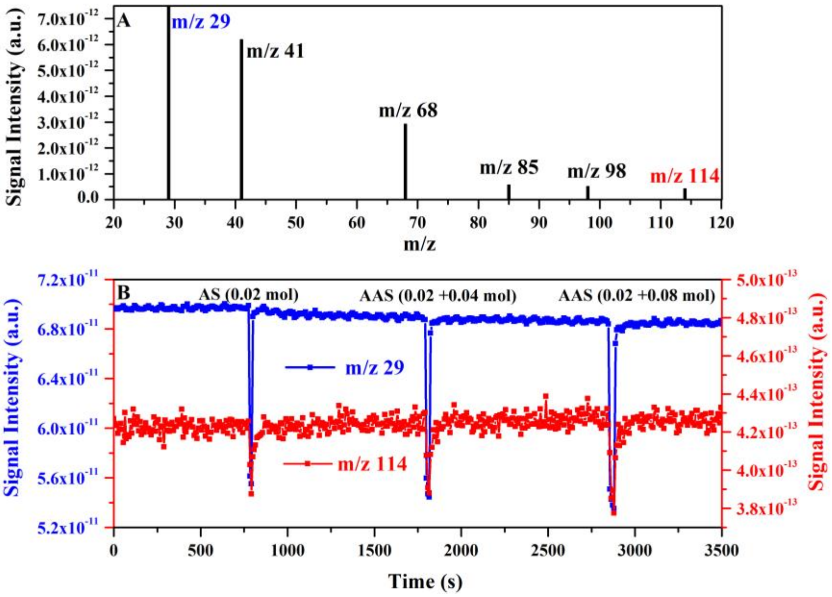

Figure S12. Mass spectrum of EM and its uptakes in AS (0.02 mol), AAS (0.02+0.02 mol), and AAS (0.02+0.04 mol) solutions.

Then, we used ATR-IR to investigate and compare the degradation of absorbed EM during its ozonolysis in the absence and presence of SO_2 to further check whether the presence of SO_2 could hamper the ozonolysis of adsorbed EM due to surface H_2SO_4 formation. 50 μL EM was first added in the Attenuated Total Reflection (ATR). At 10% RH, EM will gradually volatilize in the purge gas with the rate of 200 ml min^{-1}. Reactant gas (O_3 and SO_2) was subsequently introduced along with purge gas after liquid EM could not be observed in ATR. As shown in Figure S13, it could be found that EM consumption in the presence of SO_2 was slower than that in the absence of SO_2. This indicated that the presence of SO_2 indeed suppressed the ozonolysis of absorbed EM, which was consistent with our speculation.

This has been corrected in the revised manuscript (250-261) and Supporting Information (Line 93-109).

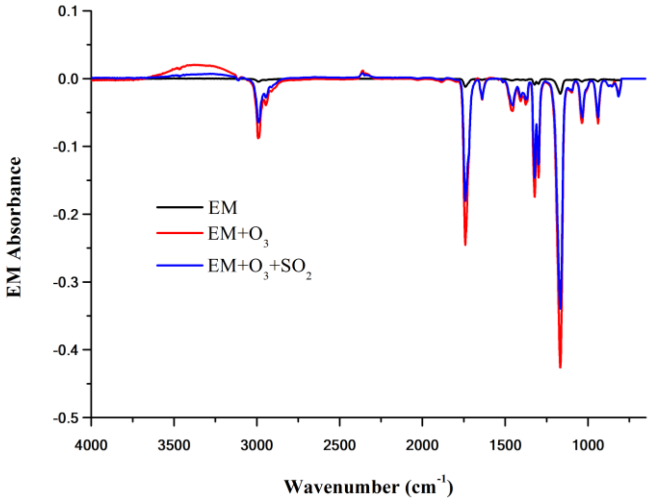

Figure S13. Absorbance of EM ozonolysis in the absence and presence of SO_2.

Q10. Lines 240-243: This is confusing, what do the authors mean?

A10. Some recent studies proved that the presence of inorganic acids HCl can may also be an effective scavenger of sCI, further suppressing the formation of low-volatility oligomers (SOA composition).(Zhao et al., 2015) The reaction between sCI and HNO_3 or HCl in particular was likely to be an important sink of sCI in polluted urban areas under dry conditions.(Foreman et al., 2016) Thus, we concluded that the surface secondary reactions between sCI and H_2SO_4 under acidity condition may also suppress the formation of low-volatility oligomers via affecting the sCI lifetime like HCl or HNO_3.

This has been added in the revised manuscript (Line 265-272).

Q11. Lines 244-248: That’s not consistent with previous works and previous studies must be discussed here. It is actually a bit concerning if the authors observed a different tendency.

A11. Previous studies on α-pinene SOA proved that the increase in particle acidity promotes or have a negligible effect on the formation of oligomers or SOA, but these studies were conducted in the absence of SO_2 rather than in the presence of

SO_2.(Kristensen et al., 2014; Iinuma et al., 2004; Han et al., 2016; Gao et al., 2004) Thus, we believe that the role of increasing seed acidity to the formation of α-pinene SOA remain controversial and need to be further investigated, especially under polluted urban areas. According to reviewer 1's comment, the description of α-pinene SOA has been deleted from the revised manuscript to make this work be better understanded.

Q12. Lines 262-264: It is not clear why the authors decided to run PMF. by looking at the results I found the discussion too qualitative and at some places even contradictory. I strongly suggest that the authors provide a simpler look at the AMS data first and then provide a more deep and consistent analyses.

A12. In the presence of SO_2, the homogeneous and heterogeneous formation of H_2SO_4 were observed to enhance and reduce SOA formation, respectively. However, whether SOA composition was also affected by the different pathway of H_2SO_4 formation remain unclear. Thus, we employed the PMF analysis to characterize and compare SOA constitution along with investigate the chemical conversion of different composition under different condition. Moreover, the contradictory discussion has been corrected in the revised manuscript.

This has been added in the revised manuscript (Line 287-290).

Q13. Finally deriving a chemical mechanism from the dataset (i.e., identifying chemical products using an AMS) presented in this manuscript appears quite speculative. Indeed, without additional evidence (e.g., additional MS data) confirming the presence of the proposed molecules in the gas and/or particle phase it is not constrained enough.

A13. Thanks for your understanding very much. A proton transfer reaction time-of-flight mass spectrometry (PTR-TOFMS) and Nitrate ion chemical ionization mass spectrometry (NO_3-CIMS) would be very necessary if we further charactering the molecule structure of proposed organic products either in the gas phase or particle phase. Unfortunately, both of above instruments were lack in our laboratory. Thus, it was very difficult to directly confirm these proposed molecules in gas and/or particle phase based on only AMS data.

This has been added in the revised manuscript (Line 483-487).

Reference

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