Interactive comment on “Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: Air quality model assessment using observations of sulfate oxygen isotopes in Beijing” by Jingyuan Shao et al.

Anonymous Referee #1

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The study of Shao et al. implemented four heterogeneous sulfate formation mechanisms into GEOS-Chem model with a focus on the low biases of modeled sulfate production rates in China. The four paths are via H2O2, O3, NO2, and TMI on aerosols. In addition, TMI-catalyzed oxidation in clouds were also considered. To reduce the uncertainties, the oxygen isotopes observations were used for comparison as it’s highly sensitive to the relative importance of different sulfate production mechanism. To investigate the dependence on aerosol PH, sensitivity studies with prescribed values of aerosol PH were also conducted. The design of the experiments are comprehensive and the results are convincing. Overall, the results with the four added heterogeneous reactions significantly reduced the low biases of sulfate and also oxygen isotopes, which show better agreement with the observations. The publication is very well written, clearly structured, and the analyses are comprehensive and convincing. In particular, the authors present a thorough analysis of the heterogeneous oxidation paths, substituting the bulk first-order uptake of SO2 (reaction probability /uptake coefficients) by a more specific calculation approach. The paper has a good chance to become an important reference for future studies on the sulfate heterogeneous reaction mechanism in China. It also has regional/global impacts. I support publication of this manuscript and have only a few small comments that may require minor revision.

1. P5 L45 Can you add some more details of the methodology of the in-cloud TMI-catalyzed aqueous-phase S(IV) oxidation? As it seemed this in-cloud TIM-relevant path is very important in polluted events.

2. P5 L45 The TMI-catalyzed oxidation path are important both in-cloud (aqueous) and on-aerosol (heterogeneous). Is there any possibility to verify the assumption of Fe and Mn treatments in the model, from the natural dust and anthropogenic emissions, solubility, ionic strength of cloud liquid water, etc.? Or if not, is it necessary to add some discussions about the uncertainty of those assumptions and the possibility of the impacts on the analysis?

3. P7 L110 The 2010_MEIC emission is used in the study, however the anthropogenic SO2 emissions has been reduced largely since 2009 thus the SO2 overestimation might be expected for Beijing. Is there any impacts/uncertainty induced by this issue?

In the Run_Het results, the TMI-relevant reactions are the most important among the four heterogeneous paths during both clean and polluted events. “In the model, the heterogeneous sulfate production rate from the TMI-catalyzed reaction is calculated as first-order uptake in SO2”. Is that relevant with the SO2 overestimation in the model?

4. P7 L120 The mass accommodation coefficients for O3 and NO2 are much lower that
5. P11 L345 It seemed the sulfate bias is reduced while the PM2.5 bias is still there. I’m just wondering is there any observational data of nitrate or ammonia available for comparison? It might give some indication of the partitioning of sulfate-nitrate. If the nitrate are well simulated or not impacted by the competition from sulfate formation, larger improvements of PM2.5 are expected?

6. P11 L349 The largest sulfate enhancements due to heterogeneous sulfate formation occur in megacities in eastern China and Sichuan Basin. For Sichuan region, is that also due to the high cloud liquid water path/RH?

7. In Run_HET, the simulated oxygen isotopes are improved in average but the median are largely underestimated. In addition to the assumption of O3 oxidation underestimation, is there any possibility of other missing paths that not taken into account? Any discussions necessary?