Response to Dr. Müller

I find this study very interesting and I can believe that heterogeneous chemistry might have a strong potential for SNA formation in very polluted conditions.

However, I have some doubts regarding the justification for the lower and upper limits used in the RH-dependent expression adopted for the uptake coefficient, γ. The values are taken from studies (K. Wang et al., 2012; Crowley et al., 2010; Shang et al. 2010; Wu et al., 2011) which all concern specifically reactions on dust particles. But haze particles in Northeastern China in winter are primarily a mixture of organic and SNA aerosols, i.e. very different aerosols. Aren't there studies on the uptake by sulfates or organic aerosols? If not, the manuscript should at the very least, state clearly that the adopted uptake coefficients are rather arbitrary – in the case of SO_2, it is chosen in order to match the observed concentrations of sulfates.

Response: We thank Dr. Müller for the insightful comments. It is correct that aerosols during haze episodes in China are mixed particles of organics, dust particles (including anthropogenic dusts), and SNA aerosols. As discussed in Sect. 2.2, we believe that heterogeneous chemistry may play important roles on SNA formation during haze conditions.

In this work, we initially took the uptake coefficient data from dust particles for the following two reasons. First, mineral composition in ambient aerosols in China can come from both anthropogenic and nature sources because of huge emissions of anthropogenic dusts (e.g., ~8 Tg anthropogenic dusts in primary $PM_{2.5}$ emissions in 2005, Lei et al., 2011). As the subsequence, high concentration of mineral compositions was observed in ambient aerosols during polluted days. For example, mineral compositions in $PM_{2.5}$ reached 101.5 μg m^{-3} on 13 Jan 2013 in Beijing (He et al., 2014). In this case, we think that taking the uptake coefficient values from dust aerosols is at least partly valid. Second, in-situ observations have found significant enhancement of SO_2 oxidation rates under wet conditions, indicating possible missing heterogeneous reactions on deliquescent particles (Zheng et al., 2014). However, the coefficients of SO_2 uptake by aerosols are only established for ice surfaces and mineral dust particles (Kolb et al., 2010). The parameterization of heterogeneous reaction of SO_2 on soot, organics, and SNA aerosols are not well established yet. We then took the uptake coefficients from reactions on dust particles and conducted several sensitivity runs by adjusting the uptake coefficients with successive approximation approach. We finally choose the value that can best match observations. We believe that this is the only way to push forward before the proposed mechanism was validated in laboratories. In the revised manuscript, we explained the reasons of using uptake coefficients from reactions on mineral dusts and presented the sensitivity analysis of uptake coefficients.

Another point concerns the abrupt increase in sulfate concentration observed in haze conditions, 70-130 μg m^{-3} in a few hours, which is presented as argument for a large heterogeneous production. Aren't meteorological variations the main driver for such large changes? Although I acknowledge that the larger fraction of SNA in the total aerosol loading is a valid argument to the enhanced SNA formation in haze conditions.

Response: We believe that the abrupt increase of SNA concentrations is mainly due to chemical production rather than meteorological variations although we agree that the stagnant meteorological condition plays an important role on heavy pollution formation. If changes in meteorological conditions dominant the abrupt increase of $PM_{2.5}$, both primary and secondary components should increase simultaneously. However, significant increase of sulfate/EC ratios was found from clean

conditions to heavily polluted periods, suggesting enhanced chemical productions. It is found that sulfate concentration increased from 3.0 μg m^{-3} to 126.5 μg m^{-3} (a factor of 40) within three hours on January 12, while element carbon concentration increased from 2.9 μg m^{-3} to 10.5 μg m^{-3} (a factor of 4) during the same time (Zheng et al., 2014). This suggests that the meteorological variation can only partly interpret the abrupt increase of sulfate concentration, while the main driver of sulfate increase should be attributed to the enhanced chemical formation process, most probably heterogeneous chemistry as discussed in Sect. 2.2.

References:

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NO_x promote the conversion of SO_2 to sulfate in heavy pollution days, Sci. Rep., 4, 4172, doi: 10.1038/srep04172, 2014.

Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George, C., Griffiths, P. T., Hanson, D. R., Kulmala, M., McFiggans, G., Pöschl, U., Riipinen, I., Rossi, M. J., Rudich, Y., Wagner, P. E., Winkler, P. M., Worsnop, D. R., and O' Dowd, C. D.: An overview of current issues in the uptake of atmospheric trace gases by aerosols and clouds, Atmos. Chem. Phys., 10, 10561–10605, doi:10.5194/acp-10-10561-2010, 2010.

Lei, Y., Zhang, Q., He, K. B., and Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990–2005, Atmos. Chem. Phys., 11, 931–954, doi:10.5194/acp-11-931-2011, 2011.

Zheng, G. J., Duan, F. K., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Su, H., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing, Atmos. Chem. Phys. Discuss., 14, 17907–17942, doi:10.5194/acpd-14-17907-2014, 2014.

Response to Referee #1

General comments

The authors used WRF and CMAQ model to simulate air quality in North China for a winter month and have described the inability of the current CMAQ model in predicting high observed inorganic aerosol concentrations. They added several heterogeneous reactions into the CMAQ model which then improved the model performance for inorganic aerosol concentrations. They also examined the impact of anomalous meteorological conditions on model predictions. While the article is well-prepared, model predictions and subsequent conclusions are direct results of the selected uptake coefficients for the heterogeneous reactions. If different uptake coefficients are selected, then model predictions and conclusions will be different.

Response: We thank the reviewer for the constructive comments to improve our article. As the reviewer pretty worries about the selection of uptake coefficients in our work (in here and specific comments #1, 3, 4, 5, and 7), we try to provide a comprehensive response to this issue here. In the responses for specific comments below, we will not repeat the explanations but point out our revisions in the revised manuscript.

In this work, we initially took the uptake coefficient data from dust particles for the following two reasons. First, mineral composition in ambient aerosols in China can come from both anthropogenic and nature sources because of huge emissions of anthropogenic dusts (e.g., ~8 Tg anthropogenic dusts in primary $PM_{2.5}$ emissions in 2005, Lei et al., 2011). As the subsequence, high concentration of mineral compositions was observed in ambient aerosols during polluted days. For example, mineral compositions in $PM_{2.5}$ reached 101.5 μg m^{-3} on 13 Jan 2013 in Beijing (He et al., 2014). In this case, we think that taking the uptake coefficient values from dust aerosols is at least partly valid. Second, in-situ observations have found significant enhancement of SO_2 oxidation rates under wet conditions, indicating possible missing heterogeneous reactions on deliquescent particles (Zheng et al., 2014). However, the coefficients of SO_2 uptake by aerosols are only established for ice surfaces and mineral dust particles (Kolb et al., 2010). The parameterization of heterogeneous reaction of SO_2 on soot, organics, and SNA aerosols are not well established yet. We then took the uptake coefficients from reactions on dust particles and conducted several sensitivity runs by adjusting the uptake coefficients with successive approximation approach. We finally choose the value that can best match observations. We believe that this is the only way to push forward before the proposed mechanism was validated in laboratories.

In the revised manuscript, we explained the reasons of using uptake coefficients from reactions on mineral dusts and presented the sensitivity analysis of uptake coefficients. The uncertainties of uptake coefficients are evaluated through four sensitivity runs. We found that all sensitivity runs can reproduce the enhancement of relative contribution of SNA from clean days to polluted days, which further confirms the role of heterogeneous chemistry on haze formation. Based on the analysis above, we believe that our main conclusion (important role of heterogeneous reaction on deliquescent particles on haze formation) remains valid. The uptake coefficients are still highly uncertain due to lack of measurements and laboratory studies for the uptake coefficients on different types of particles are urgently needed.

Specific comments

1. *Page 16733 - Abstract*

Abstract should be revised to clearly indicate that selection of uptake coefficients for the heterogeneous reactions is arbitrary and the use of other values over-predicts sulfate compared to observed data.

Response: See response above. The following sentence were added to the abstract: "As the parameterization of heterogeneous reaction on different types of particles are not well established yet, we first took the uptake coefficients from reactions on dust particles and then conducted several sensitivity runs to find the value that can best match observations."

2. *Page 16736, line 18 (section 2)*

Not clear about the meaning of "offline-coupled Weather Research and Forecasting (WRF) model and CMAQ 5.0.1". If the authors used WRF model to generate meteorological fields which were then subsequently used to drive the CMAQ model, then the word "coupled" is misleading. Please clearly describe how they were used.

Response: WRF model is used to generate meteorological fields which drive the CMAQ model subsequently.We have removed the word "offline-coupled" in the revised manuscript.

3. *Page 16738-16741 (section 2.2)*

I agree with the comment made by J. F. Muller and also think that the selection of the uptake coefficients is arbitrary and has subsequently resulted in improvement of model performance. The uptake coefficients in the referenced articles deal with dust not sulfate or nitrate. The article should clearly indicate that the selection of the uptake coefficients for the heterogeneous reactions is arbitrary.

Response: See response above. In the revised manuscript, we explained the reasons of using uptake coefficients from reactions on mineral dusts and presented the sensitivity analysis of uptake coefficients. The uncertainties of uptake coefficients are evaluated through four sensitivity runs.

4. *Page 16745-16749 (section 4.2-4.4)*

While the current model cannot capture the observed sulfate concentrations, the improvement of model predictions is a coincident due to the selection of the uptake coefficients.

Response: See response above.

5. *The authors have completed model simulations with higher uptake coefficients from Wang et al., 2012. The results of such simulation can be presented so that readers obtain a complete picture of the impacts of heterogeneous reactions on model predictions in China.*

Response: Accepted. Results of sensitivity runs are presented in the revised manuscript.

6. *The metal catalysis pathway can be important for enhancing wintertime sulfate concentrations (Alexander et al., 2009). The authors have not presented any comparison of predicted Fe and Mn concentrations to observed data in North China. The under-prediction of Fe and Mn can also contribute to the under-prediction of sulfate in China. The heterogeneous nitryl chloride production can also enhance winter hydroxyl level which can subsequently enhance winter sulfate (Sarwar et al., 2014). The impact of such chemistry on winter sulfate in January 2013 in North China is unknown. Chemistry and aerosols can affect meteorological conditions which can subsequently affect pollutant levels (Grell et al., 2005; Wang et al., 2012). Such effects can be especially important in highly polluted conditions. The authors have not examined the impacts of chemistry and aerosols feedback on meteorological conditions and their subsequent impact on*

pollutants. While the heterogeneous reactions with arbitrarily selected uptake coefficients enhance and improve model performance for inorganic aerosols, these additional factors are likely to further enhance model predictions.

Response: We thank the reviewer for pointing out these additional sources of uncertainties. We agree that metal catalysis pathway and heterogeneous nitryl chloride production may enhance sulfate formation during wintertime. First pathway is included in the original CMAQ although we do not have observation data to evaluate the predicted Fe and Mn in aerosols. However, we feel that this is not a critical issue in predicting SNA formation under haze condition because the metal catalysis pathway is not dependent on relative humidity (Seinfeld and Pandis, 2006). As the model can well predict sulfate concentration in clean days, the Fe and Mn concentrations may not have been significantly underestimated. Second pathway is not included in this work. In the discussion section of the revised manuscript, we discussed the uncertainties from these two pathways.

The feedbacks of aerosols reduce surface solar radiation, surface temperature, boundary layer height and photolysis rates. The feedbacks can affect pollution through two mechanisms. First, the lower boundary layer suppresses the vertical mixing and dispersion of pollutants, and thus increases their concentrations. Second, the decreased photolysis rates constrain the photochemical reactions and then reduce atmospheric oxidants and secondary aerosols. Including aerosol feedback can increase total aerosol loadings during haze conditions and improve model performance, but lead to larger enhancement of primary aerosols than secondary aerosols (Wang et al., 2014), which is opposite to the observations. Online-coupled model with heterogeneous chemistry should be developed in future work.

7. *Page 16751-16752 (section 5)*

Summary and conclusions need to be qualified to reflect that while the heterogeneous reaction can reproduce the observed data, the uptake coefficients used here are highly uncertain and the use of other available uptake coefficients leads to model over-predictions. The uptake coefficients used in this study were developed for dust particles and have been arbitrarily adopted for this study. Future studies should focus on improving the uptake coefficients for particles relevant to North China. Other potential chemical reactions and feedback of chemistry and aerosols on meteorology can also affect the model predictions which have not been examined in this study. Future studies need to explore impacts of such additional factors on model predictions.

Response: See responses above. We have revised the summary and conclusion to clarify all the above issues and state clearly the additional factors future studies should focus on.

Technical corrections

1. *Page 16734, line 29 and other pages*

Should the citation of Y. S. Wang et al., 2014 be written as Wang et al., 2014?

Response: The citation of Y. S. Wang et al. (2014) is used to distinguish with Z. F. Wang et al. (2014).

2. *Page 16740, line 23 and other pages*

Should the citation of K. Wang et al., 2012 be written as Wang et al., 2012?

Response: The citation of K. Wang et al. (2012) is used to distinguish with X. Wang et al. (2012).

3. *Page 16744, 25 and other pages*

Should the citation of L. Wang et al., 2010 be written as Wang et al., 2010?

Response: Corrected.

4. Page 16747, 22 and other pages

Should the citation of X., J. Zhao et al., 2013 be written as Zhao et al., 2013?

Response: The citation of X. J. Zhao et al. (2013) is used to distinguish with B. Zhao et al. (2013).

References:

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NO_x promote the conversion of SO_2 to sulfate in heavy pollution days, Sci. Rep., 4, 4172, doi: 10.1038/srep04172, 2014.

Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George, C., Griffiths, P. T., Hanson, D. R., Kulmala, M., McFiggans, G., Pöschl, U., Riipinen, I., Rossi, M. J., Rudich, Y., Wagner, P. E., Winkler, P. M., Worsnop, D. R., and O' Dowd, C. D.: An overview of current issues in the uptake of atmospheric trace gases by aerosols and clouds, Atmos. Chem. Phys., 10, 10561–10605, doi:10.5194/acp-10-10561-2010, 2010.

Lei, Y., Zhang, Q., He, K. B., and Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990–2005, Atmos. Chem. Phys., 11, 931-954, doi:10.5194/acp-11-931-2011, 2011.

Seinfeld, J.H., Pandis, S.N.: Atmospheric chemistry and physics: from air pollution to climate change. Wiley-Interscience, NewYork, 2006.

Wang, J., Wang, S., Jiang, J., Ding, A., Zheng, M., Zhao, B., Wong, D. C., Zhou, W., Zheng, G., Wang, L., Pleim, J. E., and Hao, J.: Impact of aerosol–meteorology interactions on fine particle pollution during China's severe haze episode in January 2013, Environ. Res. Lett., 9, doi: 10.1088/1748-9326/9/9/094002, 2014.

Zheng, G. J., Duan, F. K., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Su, H., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing, Atmos. Chem. Phys. Discuss., 14, 17907–17942, doi:10.5194/acpd-14-17907-2014, 2014.

Response to Referee #2

General Comments: This work is very meaningful and helpful to understand the formation of haze day. Adding a mechanism in model would improve the performance of model.

Response: We thank the reviewer for the kind comments.

1.The format of the citation should be unified. For example, in page 16734, line 10, Y. Wang et al., 2006 should be Wang et al., 2006.

Response: Corrected.

2. Providing the concentration of gas pollutants in haze episode would be helpful to understand the formation of haze day.

Response: Accepted. We have presented the observed SO_2 and NO_2 concentrations at the THU site in the revised manuscript.

3. Please provide more information about the uptake coefficient γ, which was adopted in this MS.

Response: In this work, we first took the uptake coefficients from reactions on dust particles and conducted several sensitivity runs by adjusting the uptake coefficients with successive approximation approach. We finally choose the value that can best match observations. We have clarified this in the revised manuscript and added a summary table of adopted γ in the supplementary information.