

Chu et al. reported the effect of NO₂ and C₃H₆ on the heterogeneous oxidation of SO₂ into sulfate on TiO₂ particles. Under dark conditions, the presence of NO₂ generally enhanced the SO₂ oxidation, whereas C₃H₆ had little influence. In contrast, the presence of NO₂ and/or C₃H₆ suppressed the sulfate formation in the presence of UV irradiation. The authors attributed these results to the competitions between NO₂ and SO₂ for surface reactive sites on TiO₂ and reactive oxygen species, and between C₂H₆ and SO₂ for reactive oxygen species. However, their arguments on the underlying mechanisms are not satisfactorily explained based on the experimental results and the mechanistic insight is lacking. The impact of this study would be incremental to the understanding of heterogeneous oxidation of SO₂ in the atmosphere. The manuscript requires major revisions before publication in ACP.

Specific comments:

The authors need to specify why TiO₂ was chosen as the target material to put this work in a more appropriate context. For instance, the line 32 on page mention “TiO₂, ..., has been widely used for studying heterogeneous photochemical reactions. What is the novelty in the present study?

In the line 2 on page 5, I don't understand the correlation between the negative peaks (consumption) of the surface hydroxyls and the SO₂ adsorption. Can you elaborate how the SO₂ adsorption causes the negative peaks?

For the comparison of experiments with SO₂ alone in the presence and the absence of UV illumination, the authors suggested the potential formation of molecularly adsorbed water, but the connection of this formation to the sulfate production is lacking. What is the role of molecularly adsorbed water in the reactions studied? The formation of adsorbed water is closely related to relative humidity (e.g., Romakkaniemi et al., 2001), but no information on relative humidity has been articulated in this work.

Romakkaniemi, S., Hämeri, K., Väkevä, M., and Laaksonen, A., *J. Phys. Chem. A*, 105, 8183–8188, 2001.

The UV illumination (Fig. 1b) significantly enhanced the sulfate formation relative to the dark experiment. The authors need to discuss what is the role of UV illumination in the enhanced sulfate formation in the paragraph starting from the line 4 on page 5. Because of the lacking discussion, the argument in the lines 11-12 on page 5 does not seem correct. High sulfate formation rates under UV illumination might also cause the disappearance of sulfite peaks in the spectra due to rapid conversion of SO₂ into sulfate.

In the lines 28-30 on page 5, the authors described that more sulfate with UV irradiation in the SO₂ + NO₂ system than without UV irradiation was consistent with the results in the SO₂ alone system. However, the mechanism might be different between the two systems. For instance, nitrate formed is subjected to photolysis under UV irradiation (> 300 nm). Recent work has found that nitrate photolysis can enhance the conversion of SO₂ into sulfate in wet aerosols (Gen et al., 2019). It would be useful if the authors provide more discussion from a perspective of the mechanisms.

Gen, M., Zhang, R., Huang, D., Li, Y., and Chan, C. K., Heterogeneous Oxidation of SO₂ in Sulfate Production During Nitrate Photolysis at 300 nm: Effect of pH, Relative Humidity, Irradiation Intensity, and the Presence of Organic Compounds. *Environ. Sci. Technol.*, 2019.

In the line 31 on page 5, it is not clear about what is the opposing effect. The authors need to clarify this effect.

The discussion in the lines 3-5 on page 7 cannot explain the suppressing effect of NO₂ on the sulfate formation under UV irradiation, relative to the SO₂ alone system. How the presence of NO₂ suppresses sulfate formation on TiO₂ under UV irradiation.

Reactive oxygen species (ROS) are seemingly responsible for the oxidation of SO₂ into sulfate. However, the lacking information here is what ROS are generated on TiO₂. The authors need to explain what are formed on TiO₂ and how the formed ROS oxidize SO₂ in the earlier part of the manuscript.

In the lines 19–21 on page 8, this discussion is purely a simple guess. What are potential products blocking the surface reactive sites? Do you have any experimental evidence to support the presence of products (e.g., in DRIFTS spectra)?

In the line 26 on page 8, what was saturated with?

In the line 11 on page 9, how can we know that NO₂ may compete with SO₂ for both surface active sites and ROS? Based on the results (Fig. 6), NO₂ appears to compete with SO₂ for the surface active sites, but not for ROS since the sulfate formation rate (increasing rate of the K-M integrated area) with the step-by-step gas (NO₂ first and then SO₂) injection in the later reaction time becomes comparable to that with both gases together.

The statement in the line 14 on page 9 is too general. Need to rewrite.

Minor comments:

In the line 30 on page 2, please specify what type of illumination the authors refer to.

Line 9 on page 4: what are the wavelengths of the UV irradiation?

Please state gas concentrations in the experimental.

I believe that the title of sub-section 3.1.3 is typo.

Line 17 on page 8: “with of” is typo.