Adsorption of SO_2 on Oxides: Decomposition Reactions and the Formation of SO_3 and SO_4

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Abstract No. Rodr7859

Beamline(s): **X19A, U7A**

Introduction: Sulfur dioxide is a major air pollutant produced by the combustion of coal and fuels derived from petroleum. In the atmosphere, SO_2 is oxidized and interacts with water to produce acid rain that kills vegetation and corrodes buildings and monuments. In addition, SO_2 poisons the catalysts that are used for the removal of CO and NO from automobile exhaust. Metal oxides are frequently employed as sorbents or catalysts for destroying SO_2.

Methods and Materials: X-ray absorption near-edge spectroscopy (XANES), photoemission (PE), and density functional (DF) calculations were used to study the chemistry of SO_2 on oxide surfaces.

Results: Our results indicate that XANES is an excellent technique for studying the chemistry of SO_2 on oxides providing clear "fingerprints" for the identification of chemisorbed S, SO_2, SO_3 and SO_4 [1-5]. The behavior of SO_2 on zinc oxide was studied in detail [1-3], examining the chemistry of the molecule on ZnO(0001)-Zn and ZnO(0001)-O single-crystal surfaces, polycrystalline ZnO films, and powders of the oxide [1-3]. On all these systems, the SO_2 molecule interacted strongly with the O sites forming SO_3 species. The interactions with the Zn sites were very weak and there was no dissociation of the SO_2 molecule. Theoretical calculations indicate that the occupied states of the cations in ZnO are too stable to interact well with the LUMO of the SO_2 (S-O anti-bonding) [1]. In general, the adsorption of SO_2 on many oxides (ZnO, MgO, TiO_2, Cr_2O_3, CuO, CeO_2) leads to formation of SO_3 or SO_4 without breaking of S-O bonds [1-5]. The cleavage of S-O bonds can be facilitated by promotion of the oxides with alkali metals [1,2]. Another pathway for the dissociation of SO_2 involves the creation of O vacancies. For example, after adsorption of SO_2 on Cr_2O_3 only sulfate is present on the system, but on Cr_2O_{3-x} a fraction of the adsorbed molecules fully decomposes producing atomic sulfur (see figure below) [5].

Acknowledgments: This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the US Department of Energy (DE-AC02-98CH10886).

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