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**Chemistry of NO<sub>2</sub> on Oxide Surfaces: Formation of NO<sub>3</sub> on TiO<sub>2</sub>(110) and NO<sub>2</sub>↔O Vacancy Interactions**

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**Introduction:** Nitrogen oxides (NO<sub>x</sub>), one of the most harmful environmental pollutants [1], are formed in automotive engines and industrial combustion systems when air is used as an oxidant agent [2]. Titania is an important component in NO<sub>x</sub> storage-reduction catalysts. Understanding of the interactions of NO<sub>2</sub> with TiO<sub>2</sub>(110) single crystals and powders of titania is very important for developing more efficient catalysts or sorbents for pollution control.

**Methods and Materials:** A single crystal TiO<sub>2</sub>(110) and polycrystalline powders of TiO<sub>2</sub> or other oxides (MgO, CeO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, ZnO) were investigated as model systems for NO<sub>2</sub> adsorption using synchrotron-based high-resolution photoemission, X-ray absorption near-edge spectroscopy, and first-principles density functional (DF) slab calculations.

**Results:** The main product of the adsorption of NO<sub>2</sub> on TiO<sub>2</sub>(110) is surface nitrate with a small amount of chemisorbed NO<sub>2</sub>. A similar result is obtained after the reaction of NO<sub>2</sub> with polycrystalline powders of TiO<sub>2</sub> or other oxides. This trend, however, does not imply that the metal centers of the oxides are unreactive toward NO<sub>2</sub>. Photoemission data and DF calculations indicate that the surface nitrate forms through the disproportionation of NO<sub>2</sub> on Ti sites ( $2\text{NO}_{2,\text{ads}} \rightarrow \text{NO}_{3,\text{ads}} + \text{NO}_{\text{gas}}$ ) rather than direct adsorption of NO<sub>2</sub> on O centers of titania. Ti<sup>δ+</sup> (δ≤3) centers present on TiO<sub>2-x</sub>(110) surfaces react readily with NO<sub>2</sub> and eventually all become oxidized or covered with nitrate. The interactions between NO<sub>2</sub> and O vacancies of TiO<sub>2</sub>(110) are complex. Electronic states associated with O vacancies interact very well with the LUMO of NO<sub>2</sub>, with a substantial Ti(3d)→NO<sub>2</sub>(6a<sub>1</sub>) electron transfer and a weakening of the N-O bonds that favors dissociation of the molecule. This changes the chemistry of NO<sub>2</sub> on TiO<sub>2</sub>(110). At the same time, the adsorbed NO<sub>2</sub> affects the thermochemical stability of O vacancies, facilitating their migration from the bulk to the surface of titania. The behavior of the NO<sub>2</sub>/titania system illustrates the importance of surface and subsurface defects when dealing with DeNO<sub>x</sub> reactions on oxides.

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