Introduction: Nitrogen oxides (NOx), 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 NOx storage-reduction catalysts. Understanding of the interactions of NO2 with TiO2(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 TiO2(110) and polycrystalline powders of TiO2 or other oxides (MgO, CeO2, Cr2O3, Fe2O3, CuO, ZnO) were investigated as model systems for NO2 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 NO2 on TiO2(110) is surface nitrate with a small amount of chemisorbed NO2. A similar result is obtained after the reaction of NO2 with polycrystalline powders of TiO2 or other oxides. This trend, however, does not imply that the metal centers of the oxides are unreactive toward NO2. Photoemission data and DF calculations indicate that the surface nitrate forms through the disproportionation of NO2 on Ti sites (2NO2,ads → NO3,ads + NOgas) rather than direct adsorption of NO2 on O centers of titania. Tiδ+(δ≤3) centers present on TiO2-x(110) surfaces react readily with NO2 and eventually all become oxidized or covered with nitrate. The interactions between NO2 and O vacancies of TiO2(110) are complex. Electronic states associated with O vacancies interact very well with the LUMO of NO2, with a substantial Ti(3d)→NO2(6a1) electron transfer and a weakening of the N-O bonds that favors dissociation of the molecule. This changes the chemistry of NO2 on TiO2(110). At the same time, the adsorbed NO2 affects the thermochemical stability of O vacancies, facilitating their migration from the bulk to the surface of titania. The behavior of the NO2/titania system illustrates the importance of surface and subsurface defects when dealing with DeNOx reactions on oxides.

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