

Surface Layer Composition of Titania under Ambient Air

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Abstract: Three different TiO₂ samples were investigated in the process of dark, UV-, and visible light desorption of surface species: prepared by dispersion of the titania single crystal, prepared by combustion of a pyrotechnic mixture in air, and commercial P25. The composition of desorption products showed the dependence of the adsorption layer state on the TiO₂ nature. The methane photodesorption was detected only for the commercial TiO₂ P25. The possible reasons for that CH₄ emission include the capturing of the complete molecules during the TiO₂ production process and photocatalytic hydrogenation of CO₂ under UV-light.

Keywords: TiO₂, adsorbed layer, photodesorption, CO₂, methane

1. Introduction

The produced titania is often stored under ambient air condition. However, the storage of a powdered TiO₂ in air may cause the formation of adsorbed layer on its surface. The composition of this layer should be dependent on the air composition which contains a number of major (O₂, H₂O, CO₂) and minor chemical compounds (CO, CH₄, H₂, etc.) and the adsorption properties of the TiO₂ surface in relation to these species.

TiO₂ is often treated at high temperature in order to clear the surface out of water and other adsorbates before experiments. Such treatment may cause the changes not only of the adsorbed layer composition but also in the surface TiO₂ lattice layer. This may lead to a complete deleting of the adsorbed layer. On the one hand, such state of titania surface is not typical of the ordinary conditions during the heterogeneous photocatalytic processes with gas phase and, moreover, with liquids. On the other hand, the composition of the adsorbed layer of the catalyst should significantly affect the experimental conditions and thus may distort the results. So, there is a practical need for monitoring of the adsorption layer state, especially in the case of a powdered sample with a high specific surface area.

This work deals with the investigation of TiO₂ samples of various preparation methods and specific surface area values in order to identify the adsorption layer composition after the TiO₂ storage ambient air.

2. Experimental

Three different TiO₂ samples were investigated in the dark, UV-, and visible light desorption of surface species: TiO₂ prepared by dispersion of the titania mono crystal, TiO₂ prepared by combustion of a pyrotechnic mixture with microparticles Ti in air, and commercial TiO₂ P25. All the samples were suspended with deionized water before being deposited onto the inner wall of the cylindrical quartz reactor. The reactor with the sample was sealed to a high vacuum setup after drying the construction at room temperature at the air for a week. Water vapors were always present in the reactor volume and CO₂ on titania surface. Therefore, the special trap volume cooled down to 173K was inserted between the reactor and the measuring volume.

2. Results and discussion

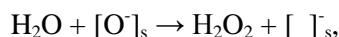
Carbon mono- and dioxide photodesorption occurs under illumination of TiO₂ with UV-light. The kinetics of desorption may be described like a fast desorption at the initial period (3-5 min) with the subsequent slow desorption at a much lower rate.

The photodesorption of methane was observed only for the commercial TiO₂ P25 in addition to CO₂ and CO photodesorption during the illumination of titania samples with UV-light. The total rate of

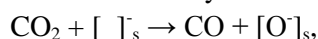
photodesorption is calculated to be $8.5 \cdot 10^{14}$ molecules/s. The nitrogen trap was used to remove CO_2 from the sampling volume for obtaining these kinetic curves.

The composition of desorption products showed the dependence of the adsorption layer state on the TiO_2 nature. The methane photodesorption was detected. The possible reasons for that methane formation include the adsorption of the complete molecules during the TiO_2 production process and (or) photocatalytic hydrogenation of CO_2 under UV-light.

A water molecule may become the reduction agent for TiO_2 surface under the light flux with the energy sufficient to overcome the TiO_2 band gap [1]. The reaction proceeds with the formation of hydrogen peroxide and the anion oxygen vacancy:



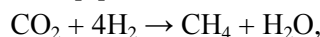
, where $[\text{O}^-]_s$ is the lattice oxygen of TiO_2 surface, and $[]_s$ denotes the anion oxygen vacancy of TiO_2 surface. In this case, the reduction of CO_2 by the anion vacancy leads to the formation of CO.



Such mechanism of CO_2 reduction over the TiO_2 surface was proposed in work [2]

The methane photodesorption from the sample surface could be a result of the TiO_2 origin. Thus, the methane was possibly adsorbed during the synthesis of the commercial P25 or during the long-term storage (the atmospheric methane concentration is about 2 ppm). In this case, the TiO_2 illumination causes the methane desorption from the surface.

The methane formation is also likely to be a result of photocatalytic CO_2 hydrogenation by hydrogen from the air (atmospheric concentration of hydrogen is about 1 ppm). The photocatalytic reaction of CO_2 and H_2 with a high yield of CH_4 was observed in work [2]:



Hydrogen can be also produced as a result of uncontrolled photocatalytic dehydrogenation of organic compounds adsorbed on TiO_2 surface [3].

4. Conclusions

Consequently, a number of reactions proceed on the surface of the commercial P25 in presence of CO_2 and H_2O .

- The reduction of TiO_2 surface by H_2O under light;
- The reduction of CO_2 with the formation of CO;
- Photocatalytic hydrogenation of CO_2 up to CH_4 by hydrogen of an unexplained origin.

References:

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