

Temperature-programmed desorption of CO₂, formed by photooxidation of CO on TiO₂ surface.

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Titanium dioxide is a widely investigated UV photocatalyst [1, 2]. The photocatalytic oxidation by TiO₂ has attracted much interest since it is useful for the transformation and decomposition of organic compounds [1, 2]. In particular the photooxidation of CO on TiO₂ is considered as the simplest reaction to study processes on catalyst surface and at the same time as ecologically significant reaction. Earlier by FTIR and TPD studies we have shown that CO₂, formed during photoreaction $\text{NO} + \text{CO} + h\nu \rightarrow \frac{1}{2} \text{N}_2 + \text{CO}_2$ on TiO₂ Degussa P25, remains on titania surface in the form of mono- and bidentate carbonates CO₃ and carboxylate CO₂⁻ species and may be removed by heating up to 500 K [3, 4]. It indicates that the products of CO photooxidation are strongly bonded to the TiO₂ surface. An interesting feature of TPD spectra of CO₂ was revealed by us that the position of the maximum of CO₂ desorption peak, T_m , (appearing in the 400 – 500 K range) shifts to lower temperature with desorbing CO₂ amount.

In present work TPD spectra of CO₂, formed on dehydroxylated TiO₂ (anatase and rutile) by photooxidation of CO, are analyzed in framework of model of desorption with two types of precursor intermediates described by R. Gorte and L.D. Schmidt [5]. Main TPD peak of CO₂ appears in the $T > 400$ K range, has a symmetric shape. A position of TPD maximum depends strongly on coverage: the CO₂ amount is lower the T_m value is higher. Such behavior of TPD CO₂ peak, which is similar to the second-order kinetic of desorption, actually may be considered as monomolecular desorption with two types of precursor states: 1) “over an empty site” and 2) “over a filled site” [5]. CO₂ desorption resulted from a migration of carbonates species along the surface (by means of the precursor state “over an empty site”) and subsequent interaction with another CO₃ species (desorption from precursor state “over a filled site”).

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References

- [1] A. Linsebigler, G. Lu, J. Yates, Jr. *Chem. Rev.*, **1995**, *95*, 735 – 758.
- [2] U. Diebold. *Surf. Sci. Rep.*, **2003**, *48*, 53 – 229.
- [3] A.A. Lisachenko, R.V. Mikhailov, L.L. Basov, B.N. Shelimov, M. Che. *J. Phys. Chem. C*, **2007**, *111*, 14440-14447.
- [4] R.V. Mikhaylov, A.A. Lisachenko, B.N. Shelimov, V.B. Kazansky, G. Martra, G. Alberto, S. Coluccia. *J. Phys. Chem. C*, **2009**, *113*, 20381-20387.
- [5] R. Gorte, L.D. Schmidt. *Surf. Sci.*, **1978**, *76*, 559-573.