IN SITU ИССЛЕДОВАНИЕ ФОТОСТИМУЛИРОВАННОЙ ДЕСОРБЦИИ CO НА ПОВЕРХНОСТИ ДИОКСИДА ТИТАНА МЕТОДОМ ИК-СПЕКТРОСКОПИИ

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Аннотация: В данной работе методом ИК-спектроскопии и волюметрии исследован процесс десорбции CO с поверхности титана при ультрафиолетовом облучении при комнатной температуре. Полученные экспериментальные данные показали, что УФ-облучение вызывает уменьшение количества адсорбированных молекул CO на поверхности. Кроме того, для наблюдаемого процесса были определены скорости реакции десорбции и получены их зависимости от начального давления адсорбата и интенсивности возбуждающего света. Также был предложен вероятный механизм для детального описания процесса.

Ключевые слова: десорбция, диоксид титана, монооксид углерода, ИК-спектроскопия, фотовозбуждение

IN SITU INFRARED SPECTROSCOPIC STUDY OF PHOTOSTUMULATED CO DESORPTION FROM TITANIUM DIOXIDE SURFACE

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Abstract: In this study the process of the CO desorption from the titania surface under ultraviolet irradiation at room temperature was studied by IR spectroscopy and volumetry methods. The obtained experimental data showed the UV–exposure induces the decrease in the amount of adsorbed CO molecules on the surface. Moreover, the desorption reaction rates were determined for the observed

process and its dependencies on the initial adsorbate pressure and on the light irradiance were acquired. In addition, the plausible mechanism was suggested to describe the process in details.

Key words: desorption, titanium dioxide, carbon monoxide, IR spectroscopy, photoexcitation

Introduction. Titania–based materials have long been the most common photocatalysts for both practical and scientific applications. They have found wide use in the production of solar cells and self–cleaning coatings, photocatalysts for water and air purification, food additives and medical coatings for implants [1, p. 735-757].

Many molecules have been proposed as probes to characterize material surface properties by infrared spectroscopy. Carbon monoxide is one of the appropriate molecules due to the existence of a dependence of its frequency shift for the molecule in the adsorbed state as compared to that for the non–perturbed molecule on the strength of the surface site [2, p. 311-320], [3, p. 1577, 1580-1581], [4, p. 1956]. Moreover, carbon monoxide as a Lewis base is suitable for quantifying the acid sites of the titanium surface, given that no irreversible chemical transformations occur in the "TiO_2–CO" system.

Recently, the CO desorption from titania (anatase) surface during UV irradiation and the following re–adsorption process after the irradiation termination were detected by *in situ* IR spectroscopy [5, p. 110,111]. In the present work, these found processes were studied in detail, and a plausible mechanism was proposed.

Experimental. The powdered titanium dioxide (Hombikat UV 100, 300 m^2/g) was prepared in the form of rectangular self–supported pellet measuring 11.5 mm x 11.0 mm with weight of 0.025 g and thickness of 135 μm. The pellet was placed into a special IR cell for study of molecules in adsorbed state ascribed elsewhere [5, p. 107-109]. The cell was connected to gas manifold. The pressure was directly controlled in the cell by a CTR100 capacitance manometer ($1 \cdot 10^{-3} \div 10^4$ Torr, Oerlikon Laybold Vacuum, Germany). Prior each experiment, the TiO_2 sample was exposed to the treatment procedure at 773 K in vacuum ($5 \cdot 10^{-6}$ Torr) and in oxygen (120 Torr) with following cooling down to room temperature (300 K) in the presence of oxygen.

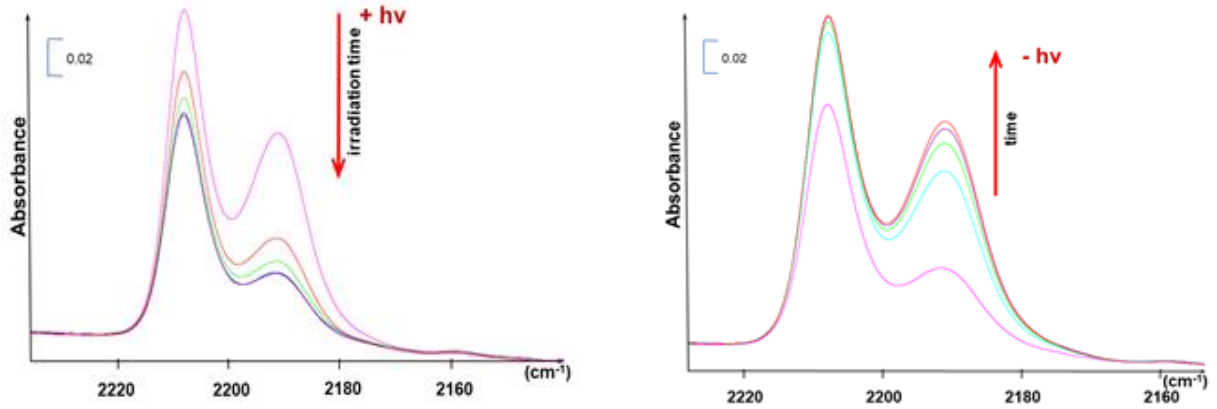
Gaseous CO (purity 99.99%, Linde Gas Rus, Russia) was introduced into the cell at various equilibrium pressures ranging of 0.04÷6.00 Torr. The amount of adsorbed CO molecules was estimated volumetrically using the Clapeyron equation

[6, p. 249]. A linear coefficient of proportionality between the number of adsorbed molecules and the IR peak area was also determined.

The used cell with dual–beam configuration enables us to register IR spectra of the sample with simultaneous sample irradiation at room temperature (300 K) [5, p. 111]. A high pressure mercury lamp equipped with an 8–cm water filter and a UFS–2 band–pass UV filter was used as the light source. The maximum irradiance at 365 nm was found to be 1.56 mW/cm^2.A set of non–selective metal–supported quartz filters that attenuate the intensity of light in the spectral range under study was used to obtain the dependence on the light intensity.

During *in situ* photo–experiments, IR spectra were registered by a ThermoNicolet *i*s-50 research–grade FT–IR spectrometer in the 900÷8000 cm^{-1} spectral region with resolution of 4 cm^{-1} by accumulating of just one scan for each spectrum. It was found that this approach does not lead to a noticeable deterioration in the quality of the obtained spectra. All experiments were performed at ambient temperature (300 K).The original spectra were analyzed by the Omnic software. Origin 2018 package was also used to examine experimental data.

Results and discussion. The obtained infrared spectra of adsorbed CO indicate the presence of two bands at 2210 cm^{-1} and 2193 cm^{-1}. According to previously published works, these bands correspond to two differently low–coordinated titanium adsorption sites [5, p. 110], [7, p. 7698-7699], [8, p. 3376].



(a) (b)

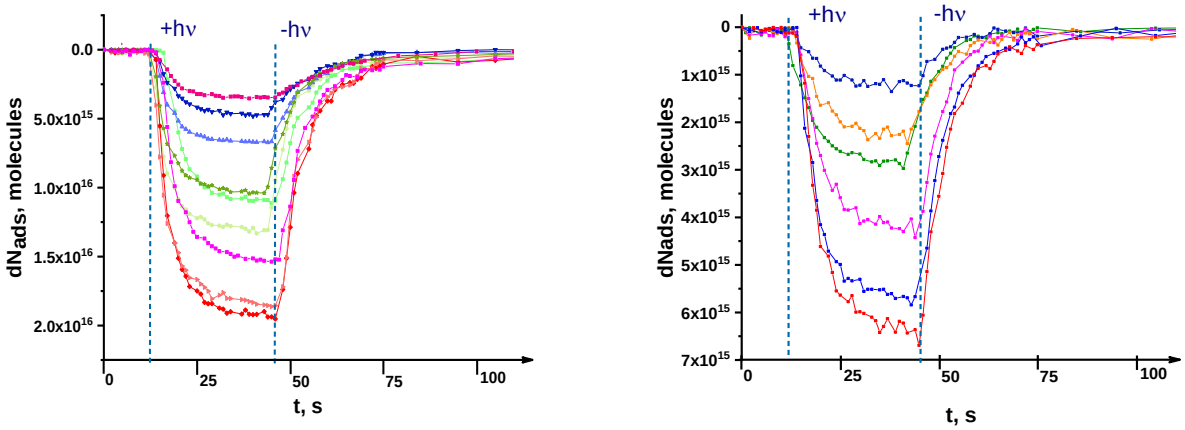
Fig. 1. *In situ* infrared spectra of CO adsorbed on TiO_2 at 300 K (a) during UV irradiation for 30 s, (b) after irradiation termination for 100 s

(Fig. 1a) represents the typical *in situ* infrared spectra of adsorbed CO at room temperature (300 K) under UV irradiation (**λ**=365 nm) of the «TiO_2–CO» system for 30 s in the titania intrinsic absorption region (**λ**<385 nm). As can be seen, the UV

exposure led to the decrease in CO intensity bands with time. The chosen exposure time, on the one hand, enables the system to reach a quasi–equilibrium state when no noticeable changes in the band intensities were observed. On the other hand, such a time period is small enough to prevent significant thermal effect of acting light (the sample temperature remained constant). Thus, the found spectral manifestations can be explained by the light–induced CO desorption from the TiO_2 surface happened.

At the same time, it has been stated that the photoexcitation of titania in its extrinsic absorption region (**λ**>385 nm, irradiation with visible light) does not have the same effect described above. This finding allows us to conclude that namely the photoexcitation of the titania in its intrinsic absorption region is responsible for the desorption process [5, p. 111-113]. In addition, the termination of UV irradiation led to recovery of the CO band intensity over time (fig. 1b).

Two experimental series were carried out at variable conditions. In first series, the different initial adsorbate pressures (0.0887 Torr, 0.1900 Torr, 1.4297 Torr, 1.9250 Torr, 2.4159 Torr, 3.6781 Torr, 4.1320 Torr and 4. 9320 Torr) at constant light irradiance (I_0=1.560 mW/cm^2) were considered. In second one, the attenuated light irradiance (I/I_0=0.016 mW/cm^2, 0.265 mW/cm^2, 0.328 mW/cm^2, 0.562 mW/cm^2, 0.858 mW/cm^2 and 1.340 mW/cm^2) at three constant initial adsorbate pressures (0.010 Torr, 1.4400 Torr and 3.9400 Torr) varied. The kinetic dependences of adsorbed CO spectra on the CO pressure and light irradiance were further acquired from the experimental data.



(a) (b)

Fig. 2. Kinetics of adsorbed CO alteration during and after UV irradiation at (a) various initial adsorbate pressure sin the range 0.04÷6.00 Torr at light density of 1.56 mW/cm^2, (b) various attenuated light intensities of 0.016÷1.340 mW/cm^2 for initial adsorbate pressure of 1.44 Torr

The obtained dependences were presented as the kinetic changes in the number of adsorbed CO molecules (N_{ads}) with time at the different initial CO pressures at full intensity (fig. 2a) and at various normalized irradiance values (I/I_0, fig. 2b). The dependencies of dN_{ads} at the initial pressures of 0.010 Torr and 3.9400 Torr were similar to those in (fig. 2b) (not shown here)

As can be noticed from (fig. 2), the behavior of all curves is quite similar in both cases: the dramatic drop in the N_{ads} is observed after the exposure initiation, then the kinetics reaches the plateau where N_{ads} remains unchanged, and further irradiation termination leads to the partial restore in the N_{ads} value.

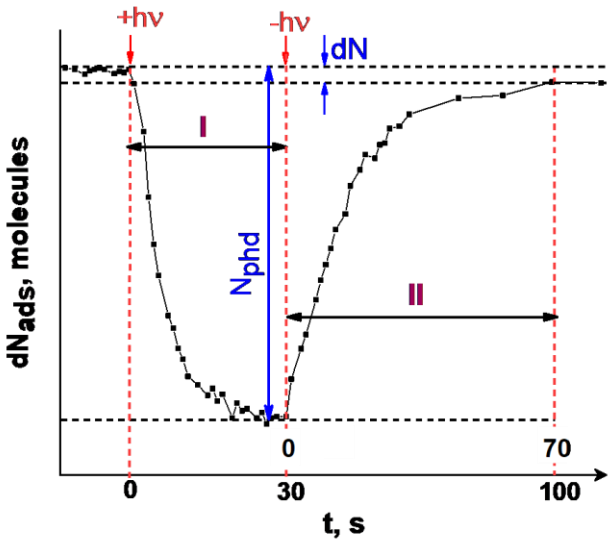


Fig. 3. The stages and parameters of the considered process

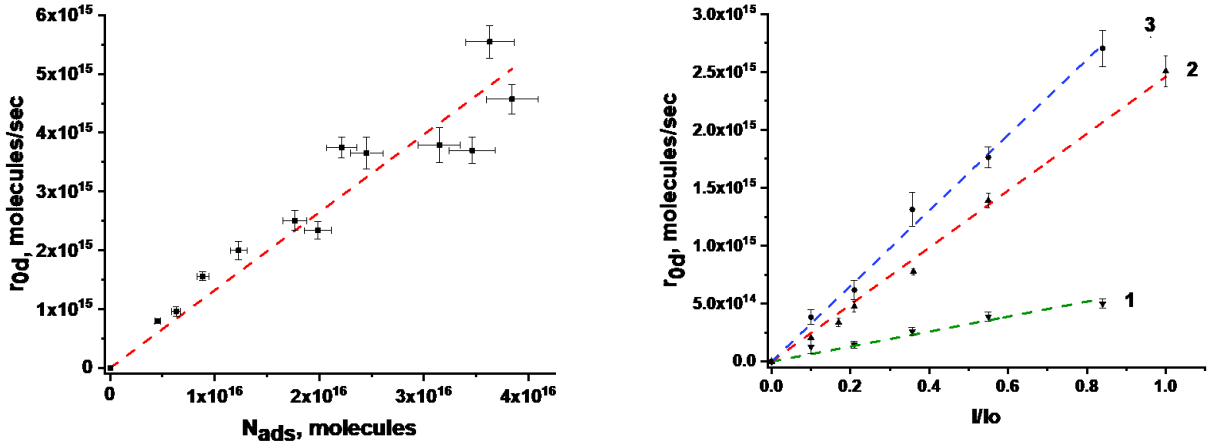
To describe the observed changes for one of the typical dependences, the scheme shown in (fig. 3) was suggested. Here the photodesorption (stage I) and re–adsorption (stage II) processes were contemplated separately. In order to characterize the stage I, the parameter that shows the decrease in the amount of adsorbed CO molecules (dN_{ads}) after 30–s irradiation (N_{phd}) was examined. At the same time, the difference between initial N_{ads} value and that at 70 s after the termination of irradiation (dN) was taken to describe the stage II process.

Thus, according to (fig. 2a), the parameter N_{phd} is proportional to the initial adsorbate pressure and can be used to determine the desorption efficiency. However, the initial desorption rate of the stage I supposed to be more appropriate characterizing parameter. So, the value of the initial desorption rate (r_{0d}) can be estimated from the kinetic approximation

$$dN_{ads} = A\exp\left(-\frac{t}{B}\right), \quad (1)$$

$$r_{0d} = \frac{A}{B}. \quad (2)$$

The obtained dependences of initial desorption rate on different initial amount of adsorbed CO at light density of 1.56 mW/cm^2 (fig. 4a) and on normalized light irradiance for three initial CO pressures (fig. 4b) can be well described by linear functions with adjusted R–square coefficient values of at least 0.97. The r_{0d} values grow with the increase in both, initial N_{ads} and I/I_0, parameters. Moreover, the rise of the curve slope with growing adsorbate pressure is noticed in (fig. 4b).



(a) (b)

Fig. 4. Initial desorption rate dependences on (a) initial amount of adsorbed CO molecules at maximal light density (I_0= 1.56 mW/cm^2) in the 0.01÷6.00 Torr pressure range, (b) normalized light intensity for various initial adsorbate pressures: 1– 0.10 Torr, 2– 1.44 Torr, 3– 3.94 Torr. Bars indicate experimental errors

Therefore, in accordance with the experimental data obtained and previous studies [9, p. 92-95], [10, p.12], the following mechanism describing the interaction between the surface of titanium dioxide and adsorbate in the observed process (stages I and II) was proposed.

In the first step, the photoexcitation of the «TiO_2–CO» system induces the electron–hole pair generation in the solid

$$\{TiO_2 \cdots CO\} + h\nu \rightarrow e + h. \quad (3)$$

The photogenerated carriers are then captured by surface active Ti^{4+} sites with adsorbed CO ($Ti^{4+\cdots}CO$), leading to the formation of Ti^{3+} sites and CO desorption

from the surface as the cation charge and, therefore, its electron–acceptor ability were decreased

$$Ti^{4+}\cdots CO + e \rightarrow \{Ti^{3+}\cdots CO\} \rightarrow Ti^{3+} + CO\uparrow. \quad (4)$$

After irradiation termination, the captured electron recombines with a hole. That results in the surface returning to its original state and CO re–adsorption on Ti^{4+} sites

$$Ti^{3+} + h \rightarrow Ti^{4+}, \quad (5)$$

$$Ti^{4+} + CO \rightarrow Ti^{4+}\cdots CO. \quad (6)$$

Moreover, the non–photostimulated adsorption–desorption also takes place during the photoprocess that is described by the equation (7)

$$Ti^{4+} + CO \leftrightarrow Ti^{4+}\cdots CO. \quad (7)$$

To confirm the validity of the proposed mechanism, our future plans include obtaining the kinetic equation for the process rate and analyzing its correspondence to the experimental dependences of the initial process rate on the adsorbate pressure and the intensity of the acting light obtained in this work. It is also necessary to elucidate the cause of the partial irreversibility of the process under study, described by the parameter dN.

Conclusions. Thus, a series of spectroscopic data was obtained to characterize CO adsorption–desorption process on the titania surface at room temperature (300 K) and the influence of UV irradiation on it. The obtained *in situ* IR spectra of adsorbed CO demonstrate the presence of two bands at 2210 cm^{-1} and 2193 cm^{-1}, that relate to the various low–coordinated adsorption centers of titanium. These data allowed us to construct the kinetic dependencies of changes in amount of adsorbed molecules (N_{ads}) at different initial CO pressures and at various normalized light intensities (I/I_0), that confirmed the fact the UV–exposure in the titania intrinsic region leads to CO desorption from its surface.

Furthermore, such parameters as the drop in the N_{ads} at 30 s (N_{phd}), the initial desorption reaction rate (r_{0d}) and the difference between N_{ads} at the initial moment of time and at 70 s (dN) were suggested to describe the desorption and re–adsorption processes effectively.

Further dependencies of the initial desorption rate on the initial adsorbate pressure and on the normalized light irradiances show the direct proportionality between the considered parameters.

The mechanism proposed is based on interaction between electrons (holes) and surface titanium sites that reduces (recover) its charge and induces CO desorption

(re–adsorption) from the titania surface. Thereby, the mechanism corresponds to the experimental data obtained but requires for the mathematical description.

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