PHOTOOXIDATION OF DONOR MOLECULES ON THE SURFACE OF BN

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It has been provided photochemical reactions with participation of photoadsorbed O_2 on the surface of hexagonal BN. It has been found that the region of photoadsorption specter is the same with the photooxidation one. The photoadsorption and photooxidation processes take place on the same photoactive center of solid and both of these processes occurs owing to photoexcitation of this center. The NO forms during photooxidation processes, which do not takes place only in the absence of light. The life time of excited oxygen is lower than that of the oxygen photoadsorption centers by an order of magnitude. The initial velocity of photoadsorption of H_2 decreases with increase of concentration of one of the reagents.

Key words: Photoadsorption, boron nitride, hole centers, photooxidation, donor molecules.

The photochemical processes with participation of H_2, O_2, CH_4 and etc. for more of oxides and alkaline halloid compounds have been investigated [1-3]. But A_3B_5 type compounds haven't been examined as a photocatalytic active object earlier. The results of investigations of photochemical reactions with participation of photoadsorbed O_2 on the surface of disperse samples of hexagonal boron nitride are given in this work.

The object and method of investigations were described in [4]. The products of photooxidation were analysed by mass-spectroscopic, manometric and thermodesorption (TD) methods. The pressure of used donor gases H_2, C_2H_6, CH_4 was P~l Pa.

Two possible variants of photooxidation reactions were established. In first case BN was radiated by light with mixture of donor gases H_2, C_2H_6, CH_4, and O_2. In second case O_2 preliminarily photoadsorbed on the surface of BN and then this system was radiated in the presence of donor gases. In first case the reaction of oxidation takes place with a constant velocity up to a complete use of compounds. The second reaction takes place with decrease of donor gas pressure. In this case the more preliminarily photoadsorbed oxygen the more the absorbed gas quantity (fig. 1).

By the TD analyze method was determined that the quantity of O_2, remaining on the surface decreases with absorbed donor gas one (fig. 2).

Under the heating from the TD spectrum disappear zones, corresponding to molecules with a small binding energy. Then heating up to 7OOK temperatures show that absorbed donor molecules can't excreted to gas phase, but only the products of there photooxidation (H_2O, CO_2 and etc.) have been observed. This means that photooxidation of donor molecules takes place owing to repited photoexcitation preliminarily photoadsorbed O_2. The first stage of photooxidation is photoadsorption of O_2 (1) and the second one is repeated photoexcitation of unactive O_2. In dark (2):

$$K + O_2 + h\nu_1 \rightarrow O_2 + K \qquad (1)$$
$$K + O_2 + h\nu_2 \rightarrow O_2^* + M \rightarrow \text{product} + K \qquad (2)$$

where K is photocatalysator, M is donor gas in gas phase, O_2 and O_2* are unactive and active forms of photoadsorbed O_2, $h\nu 1$ and $h\nu_2$ are corresponding energies of light.

The region of photoadsorption spectrum is the same with the photooxidation one. To our mind this means the photoadsorption and photooxidation processes take place on the same photoactive center of solid and both of these processes occurs owing to photoexcitation of this center.

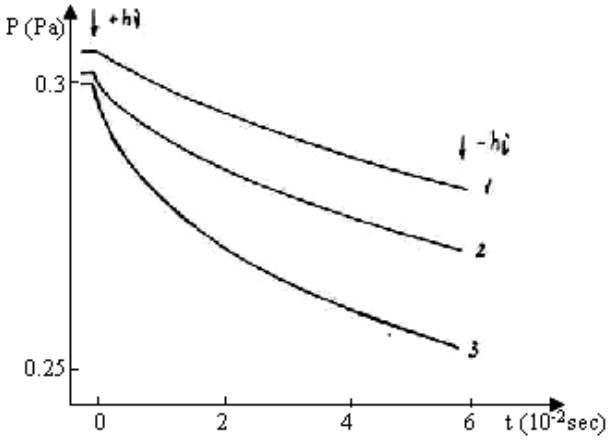

Fig. 1. The barogramms of photooxidation of H_2 (1), CH_4 (2) and C_2H_6 (3) at the same quantity of preliminarily photoadsorbed O_2 ($\Delta P_{O_2} = 5{,}7 \cdot 10^{-2}$ Pa)

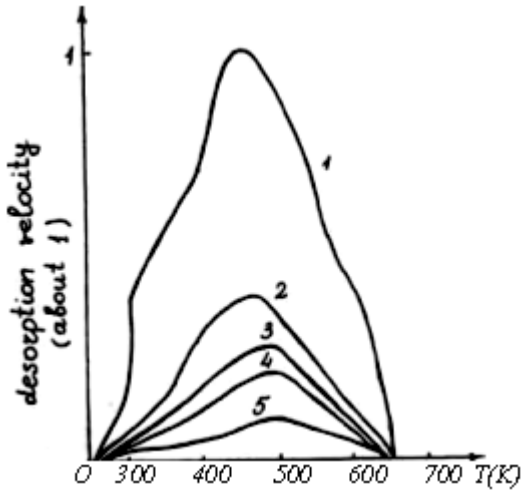

Fig. 2. TD-spectrums of photoadsorbed O_2 before (1) and after (2, 3, 4, 5) the photooxidation of C_2H_6.

TD spectrograms indicate forming also of NO during the photooxidation processes, which do not take place only on the absence of light. As a result of these processes take place partly oxidation on the surface of BN.

The life time of excited photoadsorbed oxygen has been

estimated from dependence of initial velocity of photoabsorption of H_2 on it pressure in value at the constant quantity of preliminarily photoadsorbed O_2, which is lower than that of the oxygen photoadsorption centers by an order of magnitude.

The dependence of initial velocity of photoabsorption of H2 on the quantity of preliminarily photoadsorbed O_2 has been investigated. The initial velocity decreases with increase of concentration of one of the reagents. The dependence is explained by a partial adsorption of photoadsorbed oxygen on the hole centers which are the photoadsorption centers for H_2 and blocks their for H_2 adsorption.

Thus observed effect is the result of addition of two processes: decreasing of photoadsorption velocity from blocking of some centers and increasing of photoabsorption velocity from increasing of concentration of photosorbed and photoexcitated O_2.

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BN SƏTHİNDƏ DONOR MOLEKULLARININ FOTOOKSİDLƏŞMƏSİ

Fotoadsorbsiya olunmuş O_2 molekulunun iştirakı ilə heksaqonal quruluşa malik nitrid borun səthində fotokimyəvi reaksiyalar aparılmışdır. Müəyyən edilmişdir ki, fotooksidləşmə effektinin spektral təsir oblastı fotoadsorbsiyanın spektral oblastı ilə üst-üstə düşür. Fotoadsorbsiya və fotooksidləşmə prosesləri bərk cismin səthində eyni mərkəzlərin fotohəyəcanlanması hesabına baş verir. O_2 molekulunun fotoadsorbsiyası və O_2 postsorbsiya olunmuş sistemin şüalanması zamanı TD–spektrdə NO-ya uyğun zolaq aşkar olunmuşdur. Fotoadsorbsiya olunmuş O_2-nin aktiv formasının yaşama müddəti fotoadsorbsiya mərkəzlərinin yaşama müddətindən bir tərtib kiçikdir.

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ФОТООКИСЛЕНИЕ ДОНОРНЫХ МОЛЕКУЛ НА ПОВЕРХНОСТИ НИТРИДА БОРА

Проведены фотохимические реакции с участием фотосорбированного O_2 на поверхности гексагонального BN. Определено, что спектр действия эффекта фотоокисления тот же, что и для фотоадсорбции. Процессы фотоадсорбции и фотоокисления происходят на одних и тех же фотоактивных центрах твердого тела за счет фотовозбуждения этих центров. При адсорбции O_2 непосредственно в момент облучения, а также при последующем облучении системы с постсорбированным кислородом в ТД спектре появляется NO. Время жизни возбужденной формы фотоадсорбированного на порядок меньше времени жизни центров фотоадсорбции для кислорода. Начальная скорость фотопоглощения H_2 уменьшается с увеличением концентрации одного из реагентов.

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