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Diffuse Reflectance IR Spectra of Molecular Hydrogen and Deuterium Adsorbed on Zinc Oxide

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Abstract—Diffuse reflectance IR spectroscopy is used to study hydrogen and deuterium adsorption on zinc oxide at room temperature and 77 K. At room temperature, H_2 and D_2 molecules are dissociatively adsorbed with the formation of hydrides and hydroxy groups of three types. At 77 K, diffuse reflectance spectra reveal the bands from molecular hydrogen and deuterium in addition to the dissociatively adsorbed forms. The presence of several bands of stretching H–H and D–D vibrations points to the nonuniformity of adsorption sites. This nonuniformity is also confirmed by the fact that, after heating zinc oxide from 77 K to room temperature in an atmosphere of hydrogen, only an insignificant portion of adsorbed molecular hydrogen dissociates. Most of dissociatively adsorbed hydrogen is formed without a molecular precursor. The dissociation of H_2 and D_2 most likely occurs on very active adsorption species so rapidly that the molecular precursor is not observed. The bond energy in molecular deuterium precursors of dissociation estimated from the fundamental vibration frequency and the overtone of D–D vibrations suggests moderate excitation of the bond. This agrees well with the conclusion that the dissociative adsorption of hydrogen and deuterium occurs without a molecular precursor.

INTRODUCTION

Zinc oxide is the main component of catalysts for commercial methanol synthesis [1]. Specifically, it has been proposed that the first step in carbon oxide hydrogenation on these catalysts is the activation of molecular hydrogen via dissociative adsorption [2]. The activation of hydrogen by zinc oxide in olefin hydrogenation and various photoreactions has also been studied [3–5].

It has been established that the dissociative adsorption of H_2 on ZnO at room temperature occurs via at least two pathways [6–8]. The first pathway is hydrogen adsorption on the acid–base pairs Zn^{2+}–O^{2-} in the form of covalently bound zinc hydrides ZnH and OH groups observed in IR spectra. Hydrogen adsorption of this sort takes place even at the liquid nitrogen temperature and is reversible at room temperature. In this case, dissociatively adsorbed hydrogen participates in the reaction of H/D exchange in olefin hydrogenation [6].

The second pathway of dissociative adsorption occurs at an elevated temperature at a low rate and does not lead to the appearance of IR bands belonging to hydrides and hydroxy groups. This adsorption is accompanied by a change in the electric conductivity of zinc oxide and is associated with its reduction. In this case, adsorbed hydrogen atom are most likely bridging hydrides Zn··H··Zn and protons bound to oxygen via multicentered bonds. Unlike the first pathway, the second pathway produces hydrogen that is inactive in the mentioned reactions [8].

The dissociative adsorption of hydrogen via the first pathway was studied by thermal desorption coupled with IR spectroscopy [9]. It was found that adsorbed hydrogen exists in at least three forms of adsorbed species. One of them (1A) has the absorption band from hydroxy groups at 3445 cm^{-1}. Two others (1B and 1C) have a band from hydroxy groups at 3498 cm^{-1}. The bands of adsorbed hydrides at 1710 cm^{-1} coincide for all the three forms of hydrogen. Griffin and Yates [9] also found by that species 1A is removed from the surface at 173 K. Species 1B disappears at 232 K, and species 1C disappears at 279–305 K.

Various forms of dissociatively adsorbed hydrogen might correspond to the related molecular precursors of hydrogen dissociation. However, adsorbed molecular hydrogen has not been studied by IR spectroscopy. This is most likely due to some experimental difficulties, one of which is the necessity of low-temperature IR study of weakly adsorbed hydrogen. Moreover, the very high frequency of stretching vibrations of adsorbed molecular hydrogen (~4100 cm^{-1}) is in the near IR region, where the transmittance IR method is due to strong light scattering by pressed zinc oxide pellets. Therefore, H_2 and D_2 adsorption on zinc oxide was studied in this work by Fourier transform diffuse reflectance IR (DRIFT) spectroscopy. This method is much more sensitive in the near IR region than the transmittance IR method and, at the same time, it allows one to observe the bands from the stretching vibrations of hydrides and hydroxy groups and the bands from adsorbed molecular hydrogen.

EXPERIMENTAL

Zinc oxide samples used in this work were commercially available materials prepared for diffuse reflec-

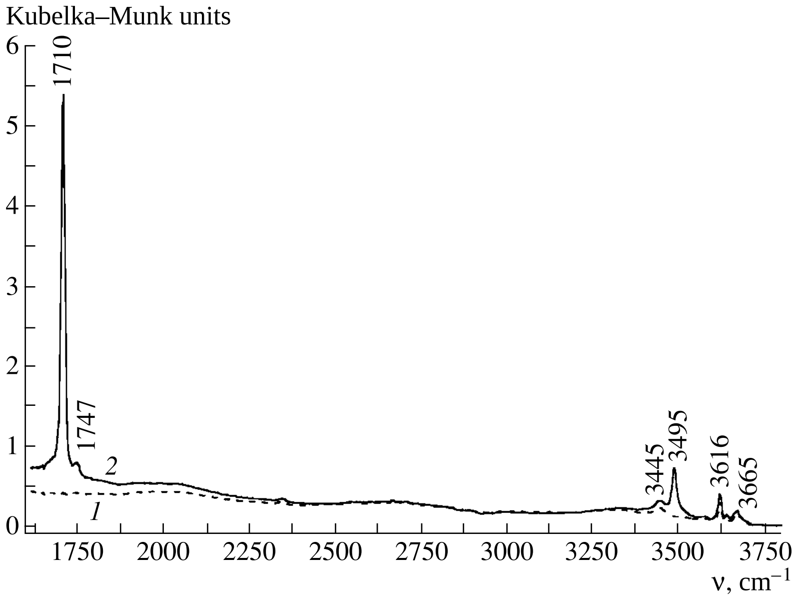

Fig. 1. IR spectrum of zinc oxide (*1*) before and (*2*) after hydrogen adsorption at room temperature. Measurements were carried out at room temperature.

tance IR measurements of hydrogen and deuterium as described below. ZnO powder was pelleted and then ground to obtain the 0.2–0.5 mm fraction. Before experiments, a sample was put into an ampule for optical measurements prepared from fused quartz where preliminary thermal treatment in a vacuum was carried out according to the following scheme. First, zinc oxide was slowly heated in a vacuum of ~10^{-4} torr to 400°C and allowed to stay under these conditions for 1 h. Then, oxygen was admitted to the ampule to a pressure of 80 torr and the zinc oxide sample was heated in oxygen at 400°C for 1 h and slowly (also for 1 h) cooled in an atmosphere of oxygen at room temperature. Then, the ampule was evacuated again.

Oxygen and hydrogen from gas bottles were purified from moisture by passing through a trap cooled with liquid nitrogen. DRIFT spectra were registered at 77 K in the range 1000–6500 cm^{-1} using a Nicolet Impact 410 IR spectrophotometer equipped with a diffuse reflectance attachment. During measurements at 77 K, the ampule with a sample was put into a quartz Dewar bottle filled with liquid nitrogen. The spectra were transformed into the Kubelka–Munk units using a standard program and assuming that the reflectance ability of zinc oxide is 0.9 at 5000 cm^{-1}. Then, the background of ZnO was subtracted from the overall spectrum. At room temperature, DRIFT measurements were carried out in quartz cells with CaF_2 windows.

RESULTS

Figure 1 (spectrum *1*) shows the room-temperature diffuse reflectance IR spectrum of zinc oxide preliminary treated in a vacuum and annealed in oxygen. In agreement with published data [6], this spectrum contains bands of hydroxyl groups at 3665, 3616, and 3445 cm^{-1}. Hydrogen adsorption at room temperature leads to the appearance of new absorption bands of zinc hydrides and hydroxy groups formed by hydrogen adsorption (Fig. 1, spectrum *2*). These data also agree with the literature [6–8]. A band at 1710 cm^{-1} corresponds to zinc hydrides, and a band at 3495 cm^{-1} corresponds to hydroxy groups. Figure 2 shows analogous data for room-temperature adsorption of molecular deuterium where the background spectrum of zinc oxide was subtracted from the overall spectrum.

Figure 3 shows the IR spectrum of zinc oxide recorded after molecular hydrogen adsorption at 77 K (spectrum *1*). According to [6], a new intense band at 3500 cm^{-1} and a less intense band at 3473 cm^{-1} belong to the stretching vibrations of hydroxy groups formed by the dissociative adsorption of molecular hydrogen. A very weak band at 4303 cm^{-1} (Fig. 4) corresponds to the composite frequency of stretching and deformational vibrations of these OH groups. The deformational frequency of hydroxy group vibrations (805 cm^{-1}) calculated from the position of this band and from the fundamental frequency of stretching vibrations agrees well with a value of 807 cm^{-1} obtained earlier [11]. Thus, the dissociative adsorption of hydrogen occurs at a high rate even at the temperature of liquid nitrogen.

Bands in the range 4000–4200 cm^{-1} are due to adsorbed molecular hydrogen. Figure 4 shows this spectral region on a larger scale. Similar to Fig. 3, line *1* in Fig. 4 corresponds to the spectrum recorded at the temperature of liquid nitrogen right after the adsorption of

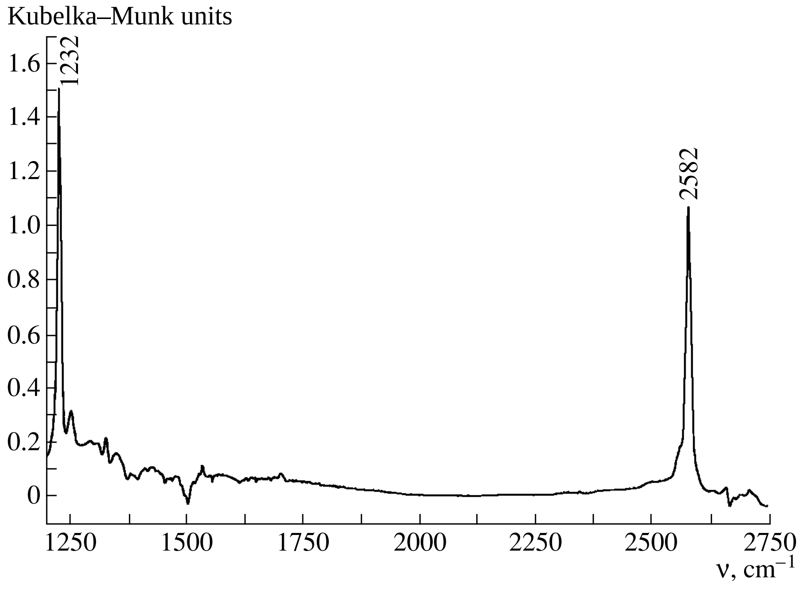

Fig. 2. IR spectrum of deuterium adsorbed on zinc oxide at room temperature. Measurements were carried out at room temperature.

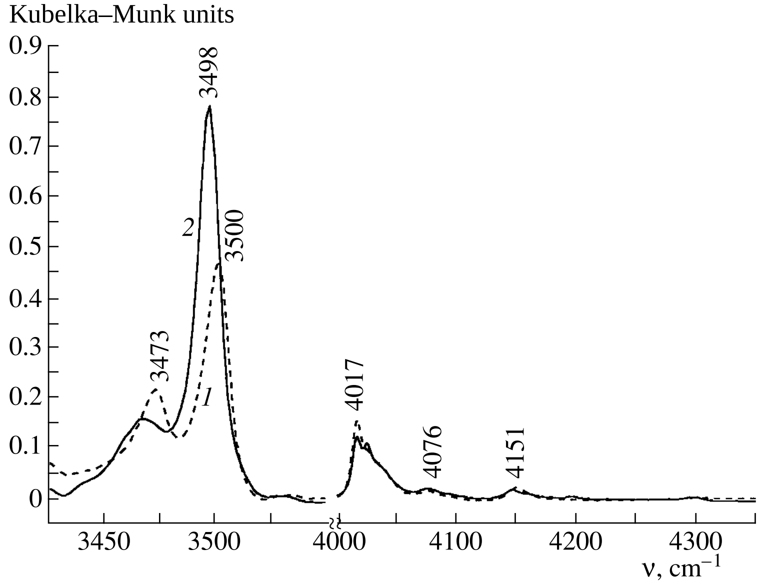

Fig. 3. IR spectrum of (*1*) zinc oxide after hydrogen adsorption at 77 K and (*2*) the same sample after its heating to room temperature in a hydrogen atmosphere. Measurements were carried out at 77 K.

molecular hydrogen, which is adsorbed in at least three or four different forms.

The first three of them associated with hydrogen adsorption on different adsorption sites correspond to the absorbance maximum of H–H stretching vibrations at 4017 cm^{-1} with poorly resolved shoulders at 4027 and 4036 cm^{-1}. As we will show below, the band at 4151 cm^{-1} is a superposition of two unresolved bands with the satellites of these bands. They correspond to the composite H–H stretching vibrations and vibrations of adsorbed hydrogen molecules around the sites of adsorption. The weak band with a maximum at 4076 cm^{-1} possibly belongs to another form of adsorbed molecular hydrogen with a satellite at 4197 cm^{-1}.

Figures 5 and 6 show analogous diffuse-reflectance spectra of deuterium adsorbed on zinc oxide. In this case, the dissociative adsorption leads to the formation of OD groups, which have bands at 2573 and 2589 cm^{-1}, and ZnD, which has a band at 1232 cm^{-1} (Fig. 2). Adsorbed molecular deuterium corresponds to bands in the range 2850–2950 cm^{-1}.

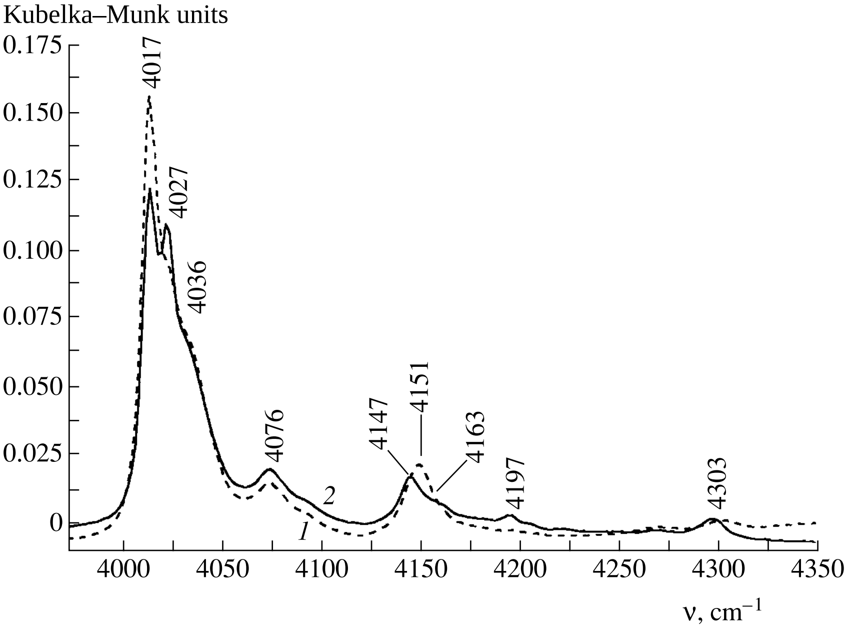

Fig. 4. IR spectrum of (*1*) hydrogen adsorbed on zinc oxide at 77 K and (*2*) the same sample after its heating to room temperature in a hydrogen atmosphere. Measurements were carried out at 77 K.

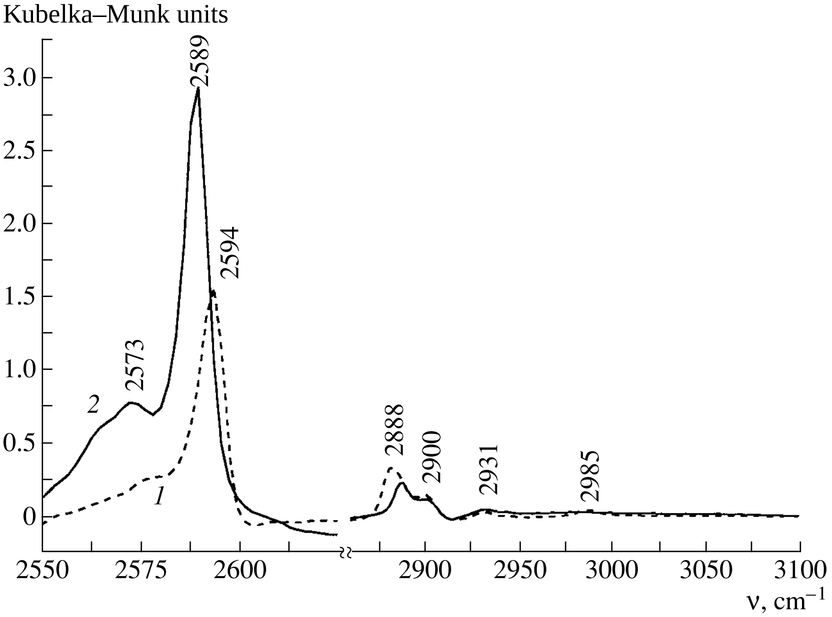

Fig. 5. IR spectrum of (*1*) zinc oxide after deuterium adsorption at 77 K and (*2*) the same sample after its heating to room temperature in a deuterium atmosphere. Measurements were carried out at 77 K.

The diffuse reflectance spectrum of molecular deuterium recorded on a larger scale is shown in Fig. 6. The most intense band at 2882 cm^{-1} in this spectrum corresponds to two unresolved bands with maximums at 4017 and 4027 cm^{-1} in the spectrum of adsorbed molecular hydrogen. The bands with maximums at 2900 and 2931 cm^{-1} correspond to the hydrogen bands with maximums at 4036 and 4151 cm^{-1}, respectively.

To determine the relationship between the molecular and dissociative forms of hydrogen adsorption, we studied repeated H_2 adsorption at the temperature of liquid nitrogen after the preliminary heating of the ZnO sample in a hydrogen atmosphere to room temperature. As can be seen from Fig. 3 (spectrum *2*), an increase in temperature to the ambient one is accompanied by the additional dissociative adsorption of hydrogen and

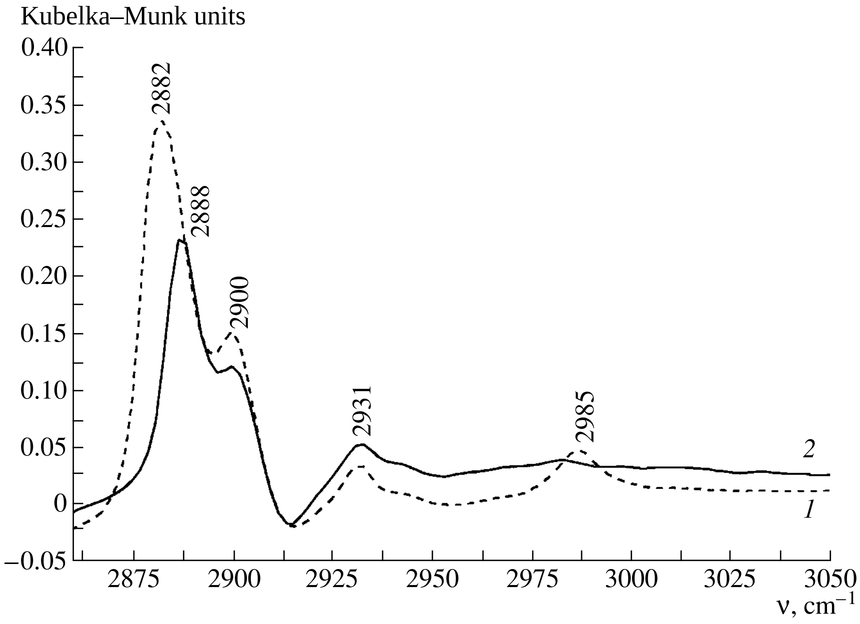

Fig. 6. IR spectrum of (*1*) deuterium adsorbed on zinc oxide at 77 K and (*2*) the same sample after its heating to room temperature in a deuterium atmosphere. Measurements were carried at 77 K.

results in about a twofold increase in the intensity of the band of hydroxy groups. Its maximum shifts from 3500 to 3498 cm^{-1}, suggesting that adsorption sites are not uniform. The band intensity at 3473 cm^{-1} also increases noticeably.

The corresponding changes occur in the diffuse reflectance spectra of adsorbed molecular hydrogen (Fig. 4). The band intensity at 4017 cm^{-1} noticeably decreases after heating the sample to room temperature and further cooling it to the temperature of liquid nitrogen. As a result, the absorption band of another band from adsorbed molecular nitrogen at 4027 cm^{-1} becomes well resolved. Simultaneously, the intensity of the band at 4151 cm^{-1} decreases, and it transforms into two poorly resolved bands with maximums at 4147 and 4163 cm^{-1}. This result supports the assignment of these bands to satellites associated with the most intense bands from the stretching vibrations of hydrogen at 4017 and 4027 cm^{-1}, respectively. Figures 5 and 6 show analogous data for deuterium adsorption.

We also found that, after an increase in the temperature to an intermediate value of 143 K and further recording the spectrum at 77 K, the intensity of the band of adsorbed molecular hydrogen at 4017 cm^{-1} decreases by a factor of ~1.5. As this takes place, the intensities of bands corresponding to both of the forms of hydroxyl groups formed also increase. However, the further heating of the sample to room temperature did not result to any additional changes in the spectrum of adsorbed hydrogen, although the intensities of bands corresponding to hydroxy groups continued to increase.

An attempt to correlate a decrease in the intensity of bands from adsorbed molecular hydrogen or deuterium and the intensity of bands of OH or OD groups formed in the dissociative adsorption failed. Indeed, Figs. 3 and 5 show that, upon heating the sample to room temperature, the intensities of bands of OH or OD groups formed in the dissociative adsorption of molecular hydrogen or deuterium almost doubled. The intensities of bands from the stretching vibrations of adsorbed molecular hydrogen or deuterium decreased to a lesser extent. It is improbable that such a difference is due to the difference in the extinction coefficients of adsorbed molecular hydrogen and the products of its dissociation. Therefore, the dissociative adsorption of hydrogen can barely be associated with the molecular hydrogen precursor reflected in the IR spectra.

DISCUSSION

The results obtained in this work suggest the presence of a wide variety of sites for molecular and dissociative adsorption on the surface of zinc oxide. In agreement with earlier data published by other authors, these sites are acid–base pairs containing coordinatively unsaturated ions of Zn(II) and the negatively charged ions of base oxygen. The nonuniformity of these sites is most likely due to different positions of acid–base pairs in atop, bridging, and hollow sites of ZnO microcrystallites. The adsorption of molecular hydrogen on these pairs is accompanied by a rather strong perturbance of adsorbed molecules.

At the same time, although a low-frequency shifts of the band of the stretching vibrations of hydrogen and deuterium with respect to the band of the gaseous hydrogen and deuterium molecules are ~140 and ~100 cm^{-1}, respectively, it can be seen that hydrogen and deuterium perturbance due to adsorption cannot explain their dissociation at 77 K. This conclusion can be drawn on the basis of the estimate of the energy of D–D bond dissociation in adsorbed D_2 molecules from the values of the fundamental frequency of deuterium stretching vibration (2886 cm^{-1}) and the overtone of these vibrations (5646 cm^{-1}).

Indeed, the fundamental frequency of deuterium stretching vibrations in the approximation of an anharmonic oscillator is described by the expression

$$\omega_{0\to 1} = \omega_e - 2\omega_e x_e,$$

and the overtone frequency is described by the expression

$$\omega_{0\to 2} = 2\omega_e - 6\omega_e x_e.$$

Therefore, for the harmonic frequency of D–D stretching vibrations ω_{eD_2} we have

$$\omega_e = 3\omega_{0\to 1} - \omega_{0\to 2} \text{ and } \omega_{eD_2} = 3026 \text{ cm}^{-1}.$$

The anharmonism coefficient is

$$x_e = \frac{\omega_{0\to 1} - \omega_e}{2\omega_e} \text{ and } x_{eD_2} = 0.023.$$

Then, using the well-known formula for the bond strength in a diatomic molecule in the Morse function approximation [11], the estimated bond strength in adsorbed deuterium molecules is

$$D = \frac{\omega_{eD_2}}{4 \cdot x_{eD_2}} = \frac{3026}{4 \cdot 0.023} = 32891 \text{ cm}^{-1}$$

$$= 4.08 \text{ eV} = 93.8 \text{ kcal/mol}.$$

On the other hand, it is known from the literature [11] that the value of the dissociation energy of free deuterium molecules is 106 kcal/mol. Thus, the energy of D–D bond dissociation decreases by ~10% upon adsorption. This is insufficient for explaining the dissociation of D_2 in the adsorbed state at 77 K with an activation energy that is close to zero.

This conclusion also agrees well with the above result, according to which most of the adsorbed hydrogen molecules observed by IR spectroscopy are not the precursors of dissociative adsorption. Indeed, as follows from our findings, heating the samples in H_2 to room temperature results in the dissociation of an insignificant portion of adsorbed hydrogen or deuterium molecules, although their main portion remains in the adsorbed molecular form. Therefore, the dissociative adsorption of H_2 and D_2 occurs on some extremely active adsorption sites at such a high rate that molecular precursors are not observed by IR spectroscopy. In this case, the IR spectra of adsorbed H_2 and D_2 are not directly relevant to the dissociative adsorption. Instead, the molecular adsorption of hydrogen and deuterium can only be used as a test that allows one to judge the presence of weaker adsorption sites on the zinc oxide surface, which do not lead to the dissociation of these molecules.

Taking this into account, our results undoubtedly indicate the strong nonuniformity of the zinc oxide surface. Indeed, in addition to three different adsorption sites for the dissociative adsorption of hydrogen, there should be three or four other sites for weaker adsorption of molecular hydrogen and deuterium, and these sites do not lead to the dissociative adsorption.

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