JOURNAL OF CATALYSIS **68**, 411–418 (1981)

Spilled-Over Hydrogen Transport from Platinum-on-Alumina Catalyst to Methoxylated Silica Aerogel

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Received May 26, 1980; revised September 22, 1980

Methoxylated silica aerogel is demethoxylated, with a loss of methane, by the spilled-over hydrogen supplied by Pt/Al_2O_3 catalyst at 430°C. The highest potential barrier for the migration of hydrogen seems to be the jump from catalyst to silica aerogel particles, whereas the transport of the spilled-over hydrogen on these particles is easy. Kinetic data account for the reaction between methoxy surface groups and probably a trihydrogen species (H_3) which would be formed by the spillover process.

INTRODUCTION

It has been shown recently (*1*) that methoxylated silica aerogel reacts at 430°C with hydrogen spilled over from a Pt/Al_2O_3 catalyst giving methane and OH surface groups. This demethoxylation provides a convenient method for the study of the migration of the spilled-over hydrogen over the silica aerogel surface. By a proper choice of the experimental conditions it should be, in principle, possible to determine the nature of the most difficult step in the hydrogen transport like the hopping of hydrogen from platinum, where the gas is first chemisorbed and dissociated, to the inorganic oxide support of the catalyst (here alumina) and then its migration over silica particles where it reacts with methoxy groups.

This paper describes the reaction of a methoxylated silica surface with atomic hydrogen generated by H_2 at an *admixed* Pt/Al_2O_3 catalyst. Mixtures prepared in a variety of ways and compositions showed different rates, from which the nature of the slow step could be determined. In all these experiments the contact between the catalyst and silica was maintained during the determinations. This type of experimentation is therefore opposed to that devised previously in the study of the unconventional catalytic properties of silica having been activated by hydrogen spillover (*2*). There the Pt/Al_2O_3 catalyst had to be removed after activation of silica by hydrogen spillover in order to record the catalytic properties of silica unscreened by the properties of Pt/Al_2O_3 catalyst (*3*).

EXPERIMENTAL

The silica aerogel (900 m^2 g^{-1}, mean particle diameter 30 Å) was prepared by hydrolysis of tetramethoxysilane dissolved in methanol. The solvent was then evacuated in an autoclave in hypercritical conditions (*4*). The surface of the aerogel is covered by methoxy groups (*1*). The kinetics of the demethoxylation of silica or of the formation of methane at 430°C was investigated in a dynamic flow microreactor (under 1 atm total pressure) equipped with a gas chromatographic unit (flame ionization detector). The concentration of generated methane in the effluent gas was monitored as a function of time and the integration of the curve obtained gave the conventional kinetic representation of the amount of the demethoxylation reaction with time. In each run 500 mg of methoxylated silica aerogel was used together with 20 mg (unless otherwise stated) of Pt/Al_2O_3

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catalyst (Pt content: 0.6%; Pt dispersion: 44%, mean particle diameter 50 Å) admixed mechanically to silica aerogel in various ways detailed below.

A flow (20 cm^3 min^{-1}) of pure gas, hydrogen, or nitrogen under 1 atm, was directed into the reactor in order to provide the second reactant (hydrogen spilled over from platinum) or to realize conditions for the blank. Two other blank experiments were made in hydrogen at 430°C but in the absence of Pt/Al_2O_3 catalyst and in oxygen at 430°C in the presence or in the absence of the catalyst. No methane was detected either by gas chromatography or by mass spectroscopy in all these blank experiments. In oxygen, with or without the catalyst, the reaction product was CO_2.

The initial amount of methoxy groups on silica was determined by carbon microanalysis of the initial aerogel (5.02% of C) and also by gravimetry in the following way. The mixture of 500 mg of silica aerogel and of 20 mg of Pt/Al_2O_3 catalyst was placed in a Cahn RH electrobalance under vacuum or in nitrogen at 430°C till a constant weight was observed. After the introduction of hydrogen (1 atm) the weight decreased to a new value because of the demethoxylation by hydrogen spillover with evolution of methane. The weight loss accounted for the presence of methoxy groups in an amount corresponding to 4.8% of C, both for nitrogen and vacuum initial conditions. The small difference between the gravimetric method and carbon microanalysis (5.02%) is due to a partial loss of methoxy groups during the thermal pretreatment of silica in nitrogen or under vacuum. The integrated amount of methane evolved by hydrogen spillover during the kinetic measurements (gc analysis) also gave the initial carbon content of 4.8%, because prior to the establishment of hydrogen flow in the reactor at 430°C the sample was heated to the reaction temperature in nitrogen flow. Three types of contact between the silica aerogel particles and the Pt/Al_2O_3 catalyst powder were realized as follows:

(i) The two powders were admixed and vigorously shaken in a container. This procedure is assumed to give a homogeneous dispersion of the catalyst powder among the silica aerogel particles. Also it fixes an average number of contacts (Fig. 1b) between catalyst particles (20 mg) and silica particles (500 mg). In a second experiment of the same type the amount of catalyst powder dispersed in silica aerogel was increased threefold (60 mg). The average number of contacts between particles of catalyst and particles of silica remained the same (loose powder) but the path for the migration of hydrogen over silica particles was decreased, as one catalyst particle "irradiated" a smaller number of silica particles (Fig. 1c). Simultaneously the concentration of active hydrogen in 500 mg of methoxylated silica batch increased by increasing the amount of the catalyst.

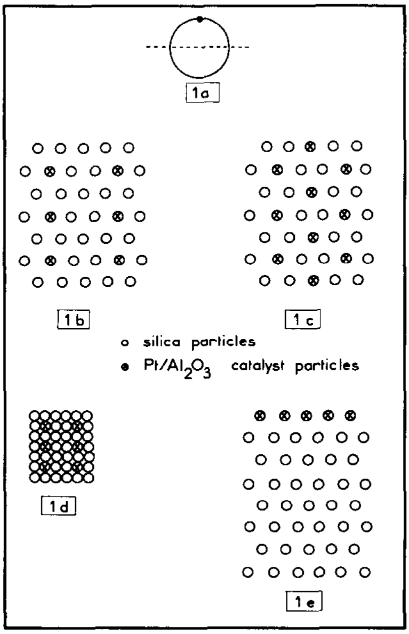

FIG. 1. (a) Compressed pellet of silica aerogel powder (65 mg) with a spot of catalyst (3 mg); (b) 500 mg of silica powder admixed with 20 mg of catalyst powder; (c) 500 mg of silica powder admixed with 60 mg of catalyst powder; (d) mixture as in (b) but compressed under 4 tons cm^{-2}; (e) separate layer of catalyst powder on the top of silica powder.

(ii) The previous type of mixture (with 20 mg of catalyst) was compressed (4 tons cm^{-2}) into the form of a pellet (Fig. 1d). This pellet was then slightly crushed in order to be introduced in the reactor. This procedure increases the number of contacts between particles and decreases the path for the migration of hydrogen over silica particles but the concentration in active hydrogen remains the same as that in the loose powder.

(iii) The uncompressed silica powder (500 mg) in the reactor (batch of a cylindrical shape, 3 cm thick, 1 cm in diameter) was covered by a thin layer (less than 1 mm thick) of 20 mg of Pt/Al_2O_3 catalyst powder (Fig. 1e). In a second experiment of this type the amount of the catalyst in the layer over silica was increased threefold (60 mg). In these experiments the average number of contacts between silica particles and the "impedance" for the migration of hydrogen from platinum to silica were the same as those in the experiments of type (i) but the path for the migration of hydrogen from the catalyst over remote silica particles (up to 3 cm distant) was considerably increased.

In all cases the reactor was flushed with nitrogen (20 cm^3 min^{-1}) during the temperature rise to 430°C and finally hydrogen flow was substituted for nitrogen flow. The initial amount of methoxy groups in nitrogen at 430°C in the silica aerogel was calculated from the 4.8% carbon content (see above) and corresponded to the total amount of methane (n_∞, in cm^3) evolved by demethoxylation by hydrogen spillover. The actual amount of methane evolved (n, in cm^3) was followed as a function of time.

Finally, infrared absorption studies of a compressed pellet of silica aerogel (65 mg) on which a small spot (ca. 1 mm diameter) of Pt/Al_2O_3 catalyst (3 mg) was included (Fig. 1a) on the border of the pellet (diameter: 20 mm) before pressing (4 tons cm^{-2}) were made at room temperature after heating the pellet to 430°C in nitrogen (initial conditions) and then in hydrogen for various lengths of time. The decrease of the intensity of the absorption band of methoxy groups (2960 cm^{-1}) in hydrogen was recorded as a function of time successively for each half of the pellet: the half-moon part containing the catalyst and the half-moon part without the catalyst (Fig. 1a). This method would detect any anisotropy in the pellet with respect to the demethoxylation of silica particles close to the catalyst and in the remote part of the pellet.

EXPERIMENTAL RESULTS

1. Kinetic Study of the Formation of Methane

The plots of ln $\{n_\infty/(n_\infty - n)\}$ are all linear (Fig. 2) and hence the reaction is first

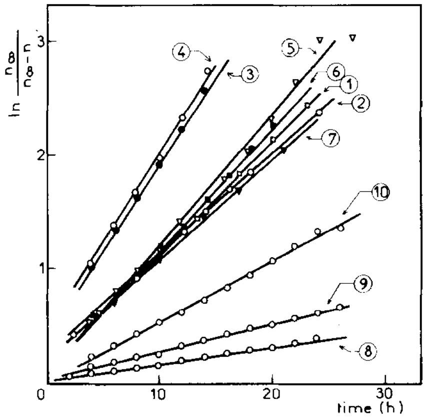

FIG. 2. First-order plot of the formation of methane from methoxylated silica at 430°C: (1) mixture of silica (500 mg) and Pt/Al_2O_3 catalyst (20 mg) particles packed according to Fig. 1b; hydrogen flow (760 Torr) of 20 cm^3 min^{-1}; (2) same type of experiment with hydrogen flow of 95 cm^3 min^{-1}; (3) mixture of silica (500 mg) and Pt/Al_2O_3 catalyst (20 mg) particles packed according to Fig. 1d (compression under 4 tons cm^{-2}); (4) mixture of silica (500 mg) and Pt/Al_2O_3 catalyst (60 mg) particles packed according to Fig. 1c; (5) separate layers of 500 mg of silica powder and 20 mg of Pt/Al_2O_3 catalyst, packed according to Fig. 1e; (6) separate layers of 500 mg of silica powder and 60 mg of Pt/Al_2O_3 catalyst, packed according to Fig. 1e; (7) same type of experiment as for curve 5 but with the reversed flow of hydrogen; (8) same type of experiment as for curve 1 but with P_{H_2} = 208 Torr; (9) same type of experiment as for curve 1 but with P_{H_2} = 300 Torr; (10) same type of experiment as for curve 1 but with P_{H_2} = 508 Torr.

order in methoxy-group concentration. The rates as given by the slopes of these plots are independent of hydrogen-flow rate between 20 and 95 cm^3 min^{-1} (see curves 1 and 2 of Fig. 2). Compression of the mixed powders (Fig. 1d) leads to an increase in rate (curve 3, Fig. 2) but the apparent activation energy (18 kcal $mole^{-1}$, 430–480°C) is unchanged. These experiments show that, even for the compressed pellet, the rate is not diffusion limited (first-order law).

The enhanced rate of the reaction for the pellet may be explained by an increased number of contacts between particles (5). More silica particles are in contact with each particle of the catalyst providing hydrogen but also the path for hydrogen over silica particles is decreased because these particles have a greater number of contacts between themselves and the distances between catalyst particles separated by silica particles are decreased. It would therefore be possible to consider two potential barriers for the availability of active hydrogen in the vicinity of OCH_3 groups. The first barrier is encountered when hydrogen has to jump from a platinum-on-alumina particle to a silica particle (the jump from platinum to alumina and from alumina to silica cannot be separated in this work). The second barrier is for the jump of hydrogen over silica particles and it depends on the average number of contacts between these particles and on the separation between catalyst particles determining the "length" of the silica particles chain.

Curve 4 of Fig. 2 shows that for a threefold increase of the amount (60 mg) of the catalyst in the loose powder (Fig. 1c) the rate of the reaction is increased. This effect may result from a decrease of the path for the migration of hydrogen over silica and from an increased concentration of active hydrogen in the batch provided by an increased amount of catalyst. Such a behaviour is always found in homogeneous or heterogeneous catalysis when the amount of catalyst varies, other conditions being conserved. It has also been observed in the spillover experiments (5). Also, in order to separate the two contributions an experiment was performed according to Fig. 1e in which the path for the migration of hydrogen from the catalyst over silica is excessively high. Curve 5 of Fig. 2 shows that the rate of reaction for 20 mg of catalyst deposited as a thin layer on the top of 500 mg of silica powder is virtually the same as that for the homogeneous dispersion of the catalyst in silica powder (curve 1 of Fig. 2). If the amount of the catalyst in the thin layer is increased threefold (60 mg) the rate is still the same as that for 20 mg of catalyst in the layer (curve 6 of Fig. 2). It would then appear that the concentration into the spilled-over hydrogen around each methoxy group on silica does not depend on the path separating Pt/Al_2O_3 catalyst from silica particles. The amount of the catalyst *in contact* with the silica batch does not increase when the thickness of a layer of catalyst on the top of silica powder (Fig. 1e) is increased threefold and the concentration into the spilled-over hydrogen is barely increased in the sample. This result also shows that it is not possible to separate the jump of hydrogen from platinum to alumina support and then from alumina to silica. The easy step, of a low potential barrier, is the migration of hydrogen, released from the catalyst particle (Pt on alumina), over silica particles and the difficult step is the jump of hydrogen from the catalyst particle to silica particles. Its frequency is increased if the number of silica particles surrounding each particle of catalyst is increased as in the case of a compressed pellet (Fig. 1d). From the kinetic point of view this effect increases the preexponential factor, as may be observed on the Arrhenius plot (not shown) giving the activation energy of 18 kcal $mole^{-1}$ both for the loose powder and for the pellet. For an increased concentration of catalyst in a loose powder (Fig. 1c) the number of contacts remains the same as that for a lower concentration of catalyst in the powder (Fig. 1b) but the concentration into the spilled-over hydrogen in the batch is increased. From the kinetic point of view the experimental rate constant (the slope of Fig. 2) is not independent of the amount of catalyst.

A rather large path for the migration of hydrogen in the experiments of Fig. 1e which does not influence the rate of reaction (the reaction proceeds with the same rate as that for the experiment of Fig. 1b) could be interpreted by the migration over silica of active hydrogen in the gas phase. If this is the case the rate of the reaction for the experiment of Fig. 1e would be decreased if the hydrogen flow, instead of being directed on the top of the sample (H_2 first meets the catalyst) which was the case for the results just described, is now reversed (H_2 first meets silica). In Fig. 2, curve 7 shows that for the experiment where the hydrogen flow passes first over silica and then only on Pt/Al_2O_3 catalyst the rate of the reaction is the same. This result is in agreement with the fact already described (Fig. 2, curve 2) concerning the insensitivity of the reaction rate to hydrogen flow rate (20 or 95 cm^3 min^{-1}). It confirms that neither the gaseous diffusion of molecular hydrogen nor that of the active hydrogen is limiting in the demethoxylation of silica. The jump of the spilled-over hydrogen from catalyst particles to silica particles does not proceed through the gas phase. If such a phenomenon does exist to some extent (*6*) the jump of hydrogen as an adsorbed species probably provides a much higher population of active hydrogen than the population of gas-phase active hydrogen and finally the first controls the rate of the reaction.

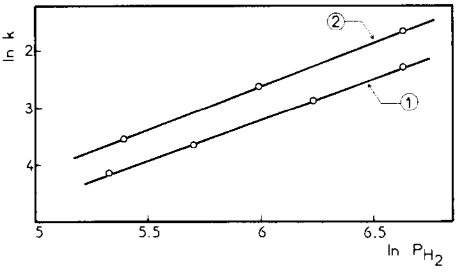

FIG. 3. The partial order with respect to hydrogen calculated from curves 1, 8, 9, and 10 of Fig. 2: (1) packing of the mixture according to Fig. 1b; (2) packing of the mixture according to Fig. 1d.

However, the partial pressure of molecular hydrogen in the gas phase may determine the concentration into the spilled-over hydrogen if this last quantity depends on hydrogen adsorption (and dissociation) equilibrium. A partial order with respect to hydrogen pressure would be observed and the rate of the reaction would show this dependence. Also the partial pressure of hydrogen in the flow was varied by dilution with nitrogen (1 atm total pressure). For partial pressures of H_2 of 208, 300, and 508 Torr in the gas flow over the mixture of loose powders (Fig. 1b) curves 8, 9, and 10 of Fig. 2 were obtained and may be compared with curve 1 established for 760 Torr of H_2. These results show that an increase of the partial pressure of H_2 increases the rate of the reaction. The order with respect to the partial pressure of this gas is determined from Fig. 3 which plots the logarithm of the slope of the straight lines 1, 8, 9, and 10 of Fig. 2 versus the logarithm of the partial pressure of hydrogen. This order is 1.45 (curve 1, Fig. 3). It has been previously shown that the diffusion of hydrogen in the compressed pellet is not rate limiting. Indeed the partial order with respect to hydrogen for the compressed pellet (Fig. 1d) is 1.49 (curve 2, Fig. 3) and is therefore practically the same as that for the loose powder.

2. *Infrared Study of the Demethoxylation of Silica*

The form of the compressed pellet of silica aerogel, containing the catalyst as a tiny spot on the edge of the pellet, is shown in Fig. 1a. The infrared absorption spectrum for each half of the pellet was recorded as a function of time of heating the pellet in hydrogen at 430°C (and also at 500°C). The blanks made on the silica pellet containing the catalyst, in nitrogen instead of hydrogen, or on the silica pellet without the catalyst but in hydrogen, did not show any decrease with time of the absorption band of OCH_3 groups, except the small initial decrease due to thermal demethoxylation (see Experimental section). The intensity of the 2960-cm^{-1} band decreased with time of demethoxylation in exactly the same way for both halves of the pellet showing that the methoxy groups in silica are removed with the same rate in the half-part of the pellet in the vicinity of the catalyst and in the half-part distant from the catalyst. This lack of anisotropy in demethoxylation is consistent with the kinetic experiments performed according to Fig. 1e and described in the previous section. It confirms also that the migration over silica of active hydrogen, provided by the catalyst, is an easy step.

As previously, the kinetic study of the demethoxylation of silica by hydrogen spillover was performed by following the decrease of the intensity of the OCH_3 band as a function of time of heating the pellet in hydrogen (at 430 and 500°C). If N is the number of methoxy groups in the pellet absorbing the infrared radiation (N_0 at time zero and N_t at time t) the Lambert–Beer law concerning the intensity I of the light transmitted at 2960 cm^{-1} may be expressed as

$$\log (I/I_0) = -\epsilon N,$$

where I_0 is the intensity transmitted when the OCH_3 groups are exhausted and ϵ is the extinction coefficient. Therefore

$$\frac{(\log (I/I_0))t = 0}{(\log (I/I_0))t = t} = \frac{N_0}{N_t}.$$

If the reaction of demethoxylation is of the first order in a constant pressure of hydrogen, as previously the reaction of the production of methane, then, is

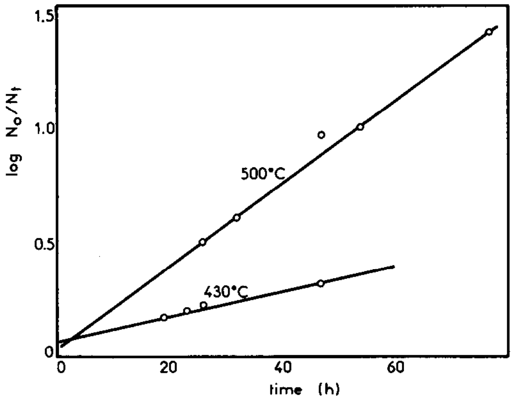

FIG. 4. First-order plot of the demethoxylation of silica followed by infrared absorption experiments (see the text) at 430 and 500°C.

$$\ln (N_0/N_t) = kt.$$

Figure 4 shows that, applying these equations, a linear plot is obtained, passing practically through the origin, for both temperatures of demethoxylation. The apparent activation energy calculated from the slopes of Fig. 4 is 20 kcal $mole^{-1}$, a value in very good agreement with that (18 kcal $mole^{-1}$) found previously for formation of methane from the mixture of silica and catalyst in a loose powder or in a compressed pellet form.

DISCUSSION

The kinetic data obtained in the dynamic reactor and by infrared experiments show that the rate of formation of methane (or of demethoxylation) may be expressed by

$$\text{rate} = k[OCH_3]P_{H_2}^{3/2}. \quad (1)$$

The apparent rate constant k depends on the amount of the catalyst and on the packing of the sample (loose powder or pellet). The first step of the reaction is very probably the equilibrated dissociative adsorption of molecular hydrogen on Pt/Al_2O_3 catalyst:

$$H_{2(g)} \rightleftarrows 2H_{(a)}. \quad (2)$$

The influence of the partial pressure of hydrogen on the rate of reaction for the samples having the same type of packing (loose powder of 500 mg of silica with homogeneously dispersed 20 mg of catalyst) may be accounted for by the dependence of the concentration in hydrogen active in demethoxylation on the pressure of molecular hydrogen:

$$H_{(a)} + H_{2(g)} \rightleftarrows H_{3(a)}. \qquad (3)$$

Because the most difficult step in the migration of hydrogen is the transport of active hydrogen from catalyst to silica it is probable that interaction (3) is operating precisely on this step. It means that dissociated hydrogen, adsorbed initially on Pt/Al_2O_3 catalyst, migrates freely in the adsorbed state (see above) onto silica as an entity $H_{3(a)}$ after it has interacted with molecular hydrogen. This last species is probably in the gas phase and not adsorbed at the high temperatures employed for the reaction. Step (3) determines a given concentration of active hydrogen on every particle of methoxylated silica powder, even in the parts fairly distant from the catalyst. The results previously described can indeed be interpreted by assuming that the concentration of active (in demethoxylation) hydrogen *on silica* depends on the concentration of the spilled-over hydrogen on *the catalyst*:

$$\underset{\text{on catalyst}}{H_{(a)}} + H_{2(g)} \rightleftarrows \underset{\text{on } SiO_2}{H_{3(a)}}. \qquad (3a)$$

Therefore

$$\frac{[H_{3(a)}]_{SiO_2}}{[H_{(a)}]_{catal.}[H_{2(g)}]} = K.$$

The concentration into hydrogen active in demethoxylation is then

$$[H_{3(a)}]_{SiO_2} = K[H_{(a)}]_{catal.}[H_{2(g)}].$$

The constant K depends on the number of points of contact between the particle of the catalyst and the particles of silica. Its value depends on the difficulty of the jump of hydrogen from the catalyst to silica. The concentration $[H_{(a)}]_{catal.}$ depends on the amount of the catalyst dispersed in silica and $[H_{2(g)}]$ depends on the pressure of molecular hydrogen. The rate-determining step is finally the interaction between $H_{3(a)}$ species and the surface methoxy group:

$$H_{3(a)} + -OCH_{3(s)} \rightarrow CH_{4(g)} + H_{2(g)} + -O-_{(s)} \qquad (4)$$

accompanied by

$$-O-_{(s)} + H_{3(a)} \rightarrow -OH_{(s)} + H_{2(g)}.$$

The rate of the determining step (4) is therefore

$$\text{rate} = k[OCH_3][H_{3(a)}]_{SiO_2}. \qquad (1a)$$

Combining Eqs. (2), (3), and (4) gives the observed rate law of Eq. (1) assuming that at the adsorption equilibrium the concentration of $[H_{(a)}]$ depends on $P_{H_2}^{1/2}$ and that of $[H_{3(a)}]$ depends on $P_{H_2} \times P_{H_2}^{1/2}$.

The existence and the stability of trihydrogen species like H_3 and H_3^+ (free, nonadsorbed) was envisaged on the basis of wave mechanics calculations (*7*). The triatomic hydrogen ion H_3^+ was found to be much more stable than the neutral triatomic molecule and its infrared absorption frequencies were calculated.

None of these were observed in our infrared experiments. The triatomic hydrogen molecule has been postulated as the intermediate complex at low temperatures in the *ortho–para* hydrogen conversion and in the exchange with deuterium (*8*) on the basis of reaction kinetics and other indirect measurements (*9, 10*). Finally surface defects (V centers) created on magnesia by thermal evacuation are centers for the adsorption of hydrogen at room temperature and below in the form of a triatomic ion, as was shown by esr spectroscopy (*11*). No esr signal was observed in our work during the hydrogen spillover experiments. It was shown before (*1*) that the number of sites accepting hydrogen on the surface of silica aerogel is of the order of $10^{12}/cm^2$. Such a low concentration would escape any present technique of investigation and only indirect methods, such as the kinetic one used in the present work, may cast some light on the nature of adsorbed hydrogen. This kinetic method is in favour of a trihydrogen species as the agent of the transport of the spilled-over hydrogen on the silica surface.

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