Adsorption of Atomic Hydrogen on Alumina by Hydrogen Spillover

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The surface species formed by adsorption of atomic hydrogen on alumina has been characterized by a desorption peak at 480°C in the temperature-programmed desorption. The atomic hydrogen has been generated either by a high-frequency discharge or by dissociative adsorption on platinum or nickel. On the alumina-supported metals hydrogen atoms formed on the metal are able to spill over onto the alumina until the alumina surface is equilibrated. From the measurement of the area of the corresponding desorption peak obtained as a function of adsorption time, pressure and temperature the values of the saturation coverage of hydrogen atoms on the alumina (2×10^{12} atoms/cm²), the coefficient of surface diffusion of atomic hydrogen on alumina at 400°C (0.9×10^{-15} cm² sec⁻¹) and the activation energy of this diffusion (28.5 kcal/mole) have been evaluated. The data obtained with two platinum on alumina catalysts with different metal dispersion agree with each other within experimental error.

1. INTRODUCTION

The surface diffusion of active species is of great interest in the understanding of kinetics and mechanisms of heterogeneous reactions. Especially in reactions on multi-functional catalysts transport phenomena may play an important role. Thus, migration of hydrogen atoms from a supported metal, which is active in the dissociative adsorption of hydrogen, to the metal carrier, which by itself has no or little activity for dissociative hydrogen adsorption, called spillover effect (*1*), has attracted considerable attention and has been the subject of several investigations (*1–14*). Although the occurrence of hydrogen spillover seems well established in a number of systems, some questions remain as to the mechanism of this surface diffusion and the nature of the migrating species.

In most previous investigations evidence for spilled over hydrogen was obtained indirectly by some sort of a topochemical reaction, e.g., the reduction of tungsten oxide (*6–8*). Earlier work in this laboratory (*9, 10*) demonstrated hydrogen spillover by an electron microscopic investigation of the reduction of an evaporated silver sulfide film, covered partly by evaporated platinum. It could be shown that hydrogen atoms generated on the platinum phase spill over the phase boundary onto a support and may diffuse over distances up to 2000 Å to a silver sulfide boundary, where reaction to H₂S and silver is occurring.

In the present work hydrogen spillover on alumina supported metals was studied directly by thermal desorption. As we described previously in a brief note (*15*) the identification of spilled over hydrogen in the thermal desorption spectrum was possible by comparison with a desorption spectrum obtained from a metal-free support, which was exposed to "atomic hy-

drogen" before desorption. Based on this method a quantitative study of the rate and amount of hydrogen spillover as a function of adsorption pressure, temperature, and time could be undertaken and the parameters of the diffusion and adsorption of atomic hydrogen (coefficient of surface diffusion, energy of activation for surface diffusion, and surface capacity of alumina for atomic hydrogen) could be evaluated.

2. EXPERIMENTAL

2.1. Apparatus

The apparatus used was a glass flow system. Nitrogen and hydrogen were purified by flowing over Cu-catalysts, silica gel, and through liquid nitrogen traps. The apparatus could be evacuated by a two-stage rotary pump, and gas flow was controlled by a needle valve. A liquid nitrogen trap prevented contamination of the catalyst by silicon grease. The sample chamber itself was made from quartz glass. Partial dissociation of hydrogen was accomplished by a high frequency discharge located in front of the adsorption zone. Temperature was measured in the catalyst bead by a Ni–CrNi thermocouple, the pressure by a Pirani gauge. A typical experiment was done in the following stages: (1) adsorption of hydrogen at given conditions (temperature, pressure, time); (2) cooling to room temperature in hydrogen (about 10 min); (3) evacuation to 10^{-2} Torr (1 Torr = 133.3 N m^{-2}) and purging with flowing nitrogen (100 Torr, 1 cm^3 sec^{-1}, 10 min); (4) temperature-programmed desorption (30 K/min) of the adsorbed hydrogen in flowing nitrogen. The hydrogen was detected with a thermal conductivity thermistor cell operating at 100 Torr. The reduced pressure was used to facilitate mass transport in the adsorbens and to increase the sensitivity of the detector. The detector was calibrated by injection of 10 μliter hydrogen through a septum located downstream of the catalyst.

2.2 Materials

The adsorption of hydrogen was studied on pure Al_2O_3–C (Degussa) and on three alumina-supported catalysts. Catalyst A, 1.0% Pt on Al_2O_3, was prepared by impregnation of Al_2O_3–C (Degussa) with chloroplatinic acid; its BET surface was 105 m^2 g^{-1} and the dispersion of platinum was 0.4 as measured by equilibrium adsorption of hydrogen at room temperature. Catalyst B was a 0.5% Pt on Al_2O_3 (Heraeus KG, Hanau) with 80 m^2 g^{-1} BET surface and 0.80 dispersion of platinum. The platinum catalysts were heated overnight in flowing hydrogen at 550°C to avoid any alteration during the experiments due to sintering. After reduction the catalysts were evacuated, heated for 2 hr in oxygen to 450°C, cooled to room temperature, and reduced once more by hydrogen. This oxidation reduction treatment was repeated after certain periods of time between the experiments.

In addition some experiments were carried with a 1.0% Ni on Al_2O_3–C (catalyst C) which was prepared by impregnation of alumina with $Ni(NO_3)_2 \cdot 6H_2O$ and reduced at 450°C for 2 hr.

3. RESULTS AND DISCUSSION

3.1 Desorption of Spillover Hydrogen

Thermal desorption curves of hydrogen from catalyst A after different adsorption treatments are shown in Fig. 1. After adsorption of hydrogen on catalyst A at 400°C and 710 Torr, the desorption spectrum showed two peaks, a large one at 130°C and a smaller one at 480°C (Fig. 1a). After adsorption at room temperature the thermal desorption shows only the large peak at 130°C (Fig. 1b), which may, however, consist of two unresolved peaks. This peak, which was also observed by other authors (16) is attributed to hydrogen dissociatively adsorbed on the platinum in agreement with experiments on unsupported platinum (17–21). In addi-
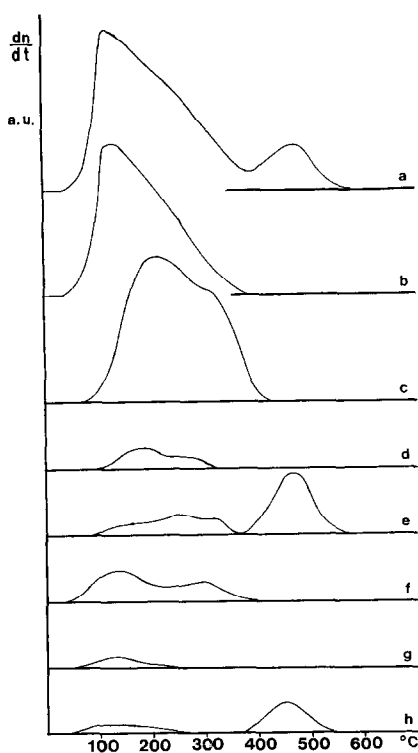
FIG. 1. Thermal desorption curves of hydrogen after the following adsorption treatment: (a) 3 hr, 710 Torr H_2 on catalyst A at 400°C, (b) 3 hr, 710 Torr H_2 on catalyst A at 25°C, (c) 3 hr, 710 Torr on platinum foil at 400°C, (d) 3 hr, 710 Torr H_2 on catalyst C at 25°C, (e) 3 hr, 710 Torr H_2 on catalyst C at 400°C, (f) 3 hr, 710 Torr H_2 on Al_2O_3 at 400°C, (g) 3 hr, 710 Torr H_2 on Al_2O_3 at 25°C, (h) 3 hr, 0.6 Torr $(H_2 + H_{atomic})$ on Al_2O_3 at 25°C.

tion, our own thermal desorption experiments of hydrogen from a platinum foil after adsorption at 400°C and 710 Torr show a similar large peak below 400°C with a somewhat changed shape (Fig. 1c).

The results of hydrogen adsorption on the nickel catalyst are quite analogous. Adsorption of hydrogen at room temperature leads to a thermal desorption spectrum (Fig. 1d) with two overlapping peaks owing to hydrogen adsorbed on nickel, as is also reported by Wedler (22). After adsorption of hydrogen at 400°C again an additional peak at about 480°C is found (Fig. 1e).

After adsorption of molecular hydrogen

on pure alumina at 400°C only two peaks at 120 and 300°C are observed (Fig. 1f) in agreement with Amenomiya (23). Furthermore adsorption of hydrogen at room temperature leads to a desorption curve (Fig. 1g), where only the peak at 120°C appears. This hydrogen adsorbed on the support cannot be seen in the desorption spectra of the supported metals because the corresponding peaks are masked by the main peaks.

The high temperature peak of Figs. 1a and e is formed neither on unsupported platinum nor on alumina after adsorption of molecular hydrogen. In order to decide whether this peak is caused by hydrogen spillover, hydrogen partly dissociated in a high frequency discharge was adsorbed on alumina at room temperature. Apart from the small peak at 120°C the thermal desorption curve in this case (Fig. 1 h) shows an additional peak at about 460°C. The desorption temperature of this peak agrees within experimental error with that of the high temperature peaks of Figs. 1a and e. Therefore we conclude that the surface species corresponding to these peaks are identical. They are only found after contact of the alumina with atomic hydrogen generated by dissociative adsorption on the metal in the first case and by high-frequency discharge in the second case.

The adsorption of molecular hydrogen to this surface state is therefore kinetically hindered up to 400°C and made possible by the presence of platinum. From the desorption temperature an activation energy of desorption of about 45 kcal/mole can be estimated. Equating this activation energy to an upper limit of the heat of adsorption the equilibrium coverage at 500°C can be calculated. This estimate shows that at this temperature adsorption of hydrogen on alumina is thermodynamically possible. Since at this temperature desorption occurs without the presence of platinum, the adsorption should also be possible because of microscopic reversibility. In fact after
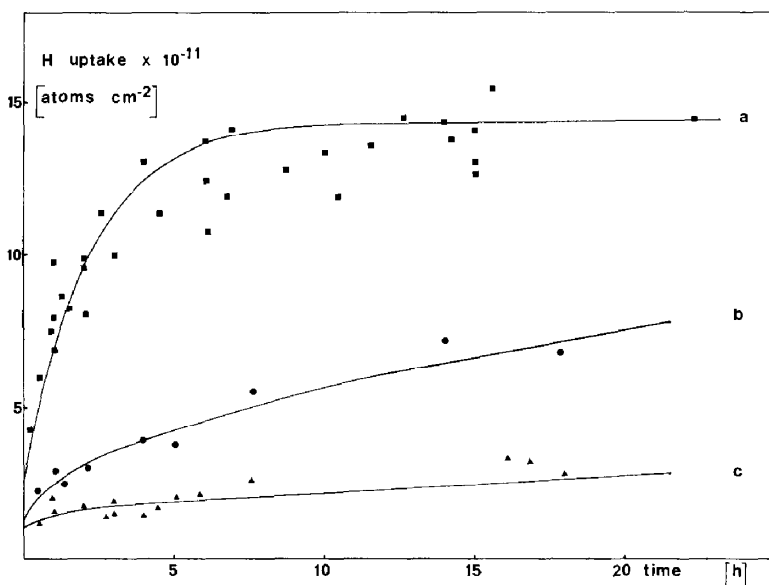
FIG. 2. Amount of spillover hydrogen versus time of adsorption at 710 Torr and (a) 400°C, (b) 320°C, and (c) 250°C on catalyst A.

adsorption of dihydrogen on alumina at 500°C and 710 Torr a small desorption peak at 480°C was observed according to formation of the corresponding surface species with molecular hydrogen. The hy-drogen uptake was found to be very small probably because the pressure used was too small to reach higher surface coverage at 500°C.

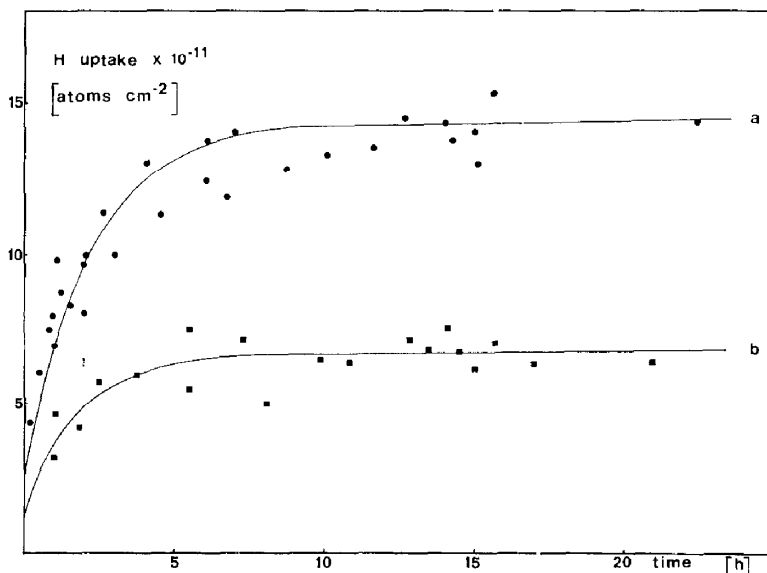Other workers (24, 25), who observed

FIG. 3. Amount of spillover hydrogen versus time of adsorption at 400°C and (a) 710 Torr and (b) 0.8 Torr on catalyst A.
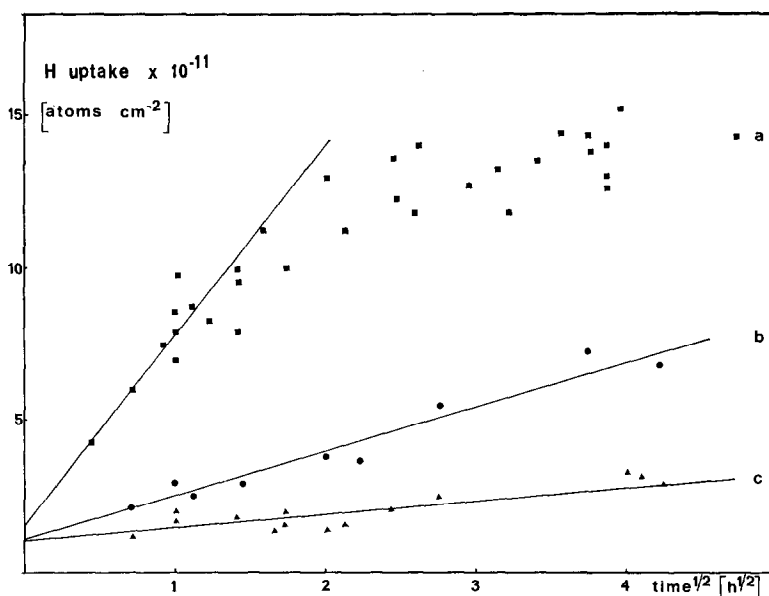
FIG. 4. Amount of spillover hydrogen versus $t^{\frac{1}{2}}$ at 710 Torr and (a) 400°C, (b) 320°C and (c) 250°C on catalyst A.

the high-temperature desorption peak after adsorption of molecular hydrogen on supported platinum, ascribed this peak to a special form of hydrogen on platinum. In view of the absence of this peak in desorption from the platinum foil under identical conditions as found here, we do not follow this interpretation.

3.2 The Diffusion of Atomic Hydrogen on the Alumina Surface

To confirm our conclusions we furthermore evaluated the amount of spilled-over hydrogen as a function of adsorption time at three different temperatures (250, 320, and 400°C) and two different pressures (0.8 and 710 Torr) at the two platinum catalysts.

The time dependence of adsorption shows qualitatively a decreasing rate of adsorption with increasing coverages. The rate increases with increasing temperature (Fig. 2) and increasing pressure (Fig. 3). The time dependence can be explained by the assumption that the dissociative adsorption of H_2 on platinum and the transfer

over the phase boundary onto the alumina is accomplished instantaneously and that the diffusion of atomic hydrogen on the alumina surface is the rate-determining step. The differential equation for surface diffusion can be solved analytically for a circular source of radius a and constant surface concentration in the source c_e (atoms cm^{-2}). The number n of hydrogen atoms diffused out of the source boundary at time t is obtained by the following equation (26)

$$n = 4 \cdot \pi \cdot a^2 \cdot c_e \cdot \left[\left(\frac{T}{\pi} \right)^{\frac{1}{2}} + \frac{T}{4} - \frac{T^{\frac{3}{2}}}{12(\pi)^{\frac{1}{2}}} \cdots \right], \quad (1)$$

where $T = Dt/a^2$ and D is the coefficient of surface diffusion of atomic hydrogen.

An analysis of Eq. 1 shows that the slope of a double logarithmic plot of n vs T, that can be seen, e.g., in the paper of Robell et al. (4), changes from 0.5 at $T = 0$ to 0.55 at $T = 0.1$ and to 0.65 at $T = 1$. Thus for a first approximation n can be

regarded proportional to $T^{\frac{1}{2}}$ and higher terms of Eq. (1) may be omitted. This simplified solution is also obtained considering a linear boundary from which diffusion starts. The amount of hydrogen diffused to 1 cm² of bare surface of alumina is given by summation of n over the number N of platinum crystallites per square centimeter of the support surface

$$c = 4N \cdot a \cdot c_e \cdot (\pi Dt)^{\frac{1}{2}}. \qquad (2)$$

In Fig. 4 the amount of spillover hydrogen is plotted vs $t^{\frac{1}{2}}$. The points fit a straight line within experimental error. The positive intercept at $t = 0$ is interpreted as the amount of hydrogen that has migrated onto the alumina immediately after the exposure to hydrogen corresponding to about 6 H atoms/crystallite for catalyst A and about 4 H atoms/crystallite for catalyst B at 400°C and 710 Torr. At the highest temperature there is a deviation from linear behavior at long exposure times. This deviation is not caused by omitting the higher terms of Eq. (1) since inclusion of these terms should give an opposite trend. However, at high coverages, which are achieved by long adsorption time and high

temperature, the assumption of diffusion from isolated sources is no longer valid, because the concentration profiles arising from the sources interfere with each other. For this case the differential equation of diffusion can be solved analytically only for line sources. If b is the distance between two such sources, one gets a solution showing that the surface concentration reaches an equilibrium value

$$c = c_e \left[1 - \frac{8}{\pi^2} \cdot \exp\left(- \frac{\pi^2 Dt}{b^2} \right) \right]. \qquad (3)$$

The continuous curves of Fig. 3 are calculated by fitted parameters of Eq. (3). The agreement of the experimental results with the values calculated from the proposed model shows that the assumptions made are reasonable.

Because equilibrium was reached only at 400°C, only the data obtained at this temperature (see Table I) were evaluated according to Eq. (3). The equilibrium surface concentration was 1.44×10^{12} cm⁻² at 710 Torr and 0.67×10^{12} cm⁻² at 0.8 Torr hydrogen pressure for catalyst A, 2.2×10^{12} cm⁻² at 710 Torr and 1.04×10^{12}

TABLE I

Data of Adsorption and Surface Diffusion of Atomic Hydrogen on Alumina

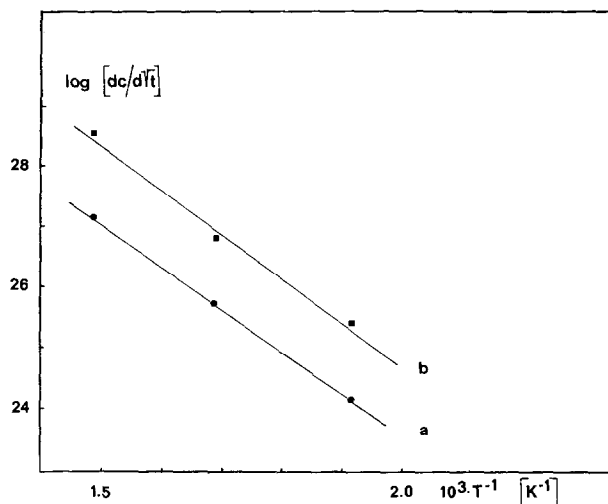|	Catalyst A	Catalyst B
Platinum content	1.0%	0.5%
Dispersion of platinum	0.4	0.8
Mean particle diameter (nm)	2.8	1.4
BET-area of support (m²/g)	105	80
Particle density	2×10^{10}	10×10^{10}
Mean distance between particles (nm)	70	31
Equilibrium coverage at 400°C and		
at 710 Torr (cm⁻²)	1.44×10^{12}	2.2×10^{12}
at 0.8 Torr (cm⁻²)	0.67×10^{12}	1.04×10^{12}
Coefficient of diffusion at 400°C and		
at 710 Torr (cm²/sec)	0.9×10^{-15}	0.95×10^{-15}
at 0.8 Torr (cm²/sec)	1.05×10^{-15}	0.8×10^{-15}
Activation energy of diffusion (kcal/mole)	28.0	29.0
Preexponential factor (cm²/sec)	1.2×10^{-6}	2.3×10^{-6}
Pt-sites/g catalyst	1.2×10^{19}	1.2×10^{19}
Al₂O₃-sites/g catalyst	1.5×10^{18}	1.8×10^{18}

FIG. 5. Arrhenius plot of $dc/dt^{\frac{1}{2}}$ at 710 Torr for (a) catalyst A and (b) catalyst B.

cm^{-2} at 0.8 Torr for catalyst B. Thus when the hydrogen pressure is increased by a factor of 900 the amount of adsorbed hydrogen increases by a factor 2.1, indicating that the saturation coverage of the alumina surface is nearly achieved. The surface capacity of alumina (1.44×10^{12} cm^{-2} and 2.2×10^{12} cm^{-2}, respectively) is very small in relation to the number of possible OH groups (2×10^{15} cm^{-2}) on the alumina surface. It is therefore assumed that the adsorbed hydrogen species is bound to definite sites such as surface defects, surface vacancies or exposed aluminum ions (27, 28). Since Al$_2$O$_3$–C contains about 0.14% Fe, surface iron ions could also act as adsorption sites. The number of these sites only depends on the preparation and pretreatment conditions of the alumina and should be constant for all adsorption temperatures investigated. Since the metal dispersions of the catalyst were known, the mean distance of platinum particles could be estimated and coefficients of surface diffusion at 400°C were evaluated (Table I). A geometric factor of 1.2 has been estimated to correct the mean distance of the platinum crystallites since for deriving Eq. (3) linear and not point sources were assumed. As in catalyst B the platinum particle density is five times greater than in catalyst A, the rate of hydrogen spillover is increased by the same factor, too, and the values of the diffusion coefficient (0.9×10^{-15} cm^2 sec^{-1}) for the two catalysts investigated agree with each other.

The experiments at lower temperatures were evaluated according to Eq. (2). As the slope of the plot of c vs $t^{\frac{1}{2}}$ is equal to $4 \cdot \pi^{\frac{1}{2}} \cdot N \cdot a \cdot c_e \cdot D^{\frac{1}{2}}$ the temperature dependence of the slope arises only from diffusion coefficient D assuming that c_e at 710 Torr is equal to the saturation coverage at 400°C and independent of temperature. Figure 5 shows a logarithmic plot of $dc/dt^{\frac{1}{2}}$ vs $1/T$ for the two catalysts. The activation energy of diffusion was calculated from this Arrhenius plot, as 28 and 29 kcal/mole, respectively. The high activation energy and the high desorption temperature of the spilled-over hydrogen indicate a rather strong chemical bond of atomic hydrogen to the surface site. Since the mean distance between two adsorption sites is about 50 Å, obviously diffusion does not occur by a simple process and more detailed information is necessary to draw conclusions from the preexponential factor.

3.3 Adsorption of Atomic Hydrogen on Alumina

The amount of spillover hydrogen taken up by alumina at 400°C after equilibration at 710 Torr is found to be 1.44×10^{12} cm^{-1} for catalyst A and 2.2×10^{12} cm^{-2} for catalyst B. From pressure dependence of the equilibrium adsorption it is seen that these values correspond nearly the saturation coverage. Though the adsorption of molecular hydrogen on alumina leads to a number of surface sites of similar magnitude (*23*, *29–31*), the surface species formed with atomic hydrogen is of different kind. Gruber (*29*) reported the existence of two kinds of adsorbed hydrogen with coverages of 1×10^{12} to 4×10^{12} atoms cm^{-2} when η-alumina was exposed at high temperatures to molecular hydrogen. Amenoniya (*23*) confirmed this by temperature programmed desorption. He found altogether five different states of chemisorbed hydrogen on γ-alumina, but only two types of chemisorption predominate above room temperature with a number of corresponding sites of 1×10^{13} cm^{-2} for either of the two types. Though similar amounts of hydrogen uptake are achieved after adsorption of either molecular or atomic hydrogen, the adsorbed hydrogen species are not identical as their desorption temperatures are different. The surface species formed from atomic hydrogen either occupy different surface sites or are bound differently to sites also concerned with molecular hydrogen adsorption. Amenomiya proposed that the sites for the adsorption of molecular hydrogen on alumina consist of pairs of defects onto which hydrogen molecules chemisorb in a quasi-atomic state with interaction between the two atoms; these pairs of sites may be occupied by a single hydrogen atom after hydrogen spillover. Desorption of hydrogen in molecular form can only occur if a single atom reacts with a surface hydroxyl group or if it migrates over the surface to another adsorbed hydrogen atom. Both mechanisms lead to a higher desorption temperature. Since in this model the surface sites are only occupied by half the amount of hydrogen, the relatively low saturation coverages obtained in this work seem to be reasonable in relation to the coverages obtained with molecular hydrogen. Furthermore the number of defects increases with increasing pretreatment temperature. For reasons of possible sintering effects supported catalysts should not be heated above 550°C and the pretreatment temperature was therefore limited.

On the other hand, sodium acetate can probably block the surface sites for adsorption of atomic hydrogen as is shown by the work of Gadgil and Gonzalez (*32*), who also obtained only small adsorption of atomic hydrogen on alumina. Pretreating the alumina with sodium acetate caused a drastically diminished adsorption of atomic hydrogen.

4. CONCLUSION

A definite proof of hydrogen spillover on alumina-supported metals was achieved by comparison of desorption spectra of hydrogen from different substrates. After adsorption of molecular hydrogen on alumina supported metals (Pt, Ni) at high temperature or after adsorption of atomic hydrogen on pure alumina peaks were found in the thermal desorption spectrum at similar desorption temperatures. These peaks do not appear after adsorption of molecular hydrogen either on unsupported platinum or on pure alumina and are therefore caused by hydrogen spillover on the supported metals. The rate of hydrogen spillover increases with hydrogen pressure, adsorption temperature, and metal dispersion. The amount of spilled-over hydrogen is proportional to the square root of adsorption time at low coverages and reaches a limiting value at high temperature and long adsorption time.

The mechanism proposed to interpret

the experimental data includes fast dissociative adsorption of hydrogen on the metal and fast spillover of atomic hydrogen over the phase boundary to the alumina. The surface diffusion of atomic hydrogen on alumina is supposed to be the rate-limiting step. From the evaluation of the data according to the proposed model the coefficient of diffusion of atomic hydrogen on the alumina surface at $400°C$ $(0.9 \times 10^{-15}$ cm^2 $sec^{-1})$, the activation energy of diffusion (28 to 29 kcal $mole^{-1}$), and the surface capacity of the alumina for atomic hydrogen $(1.5$ to 2×10^{12} $cm^{-2})$ were calculated.

ACKNOWLEDGMENTS

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