NOTES

The Effect of Water on Hydrogen Thermodesorption from the Surface of Rh/γ-Al$_2$O$_3$ Catalysts

Adsorbed water has been found to affect greatly hydrogen thermodesorption from Rh/Al$_2$O$_3$ catalysts. Water formed during H$_T$–O$_T$ titration and that introduced from outside give eventually analogous changes in hydrogen temperature-programmed desorption curves. As the amount of water increases the amount of desorbed hydrogen initially increases and then decreases. It seems that changes in hydrogen thermodesorption are a symptom of metal–support interaction. A model of this interaction has been suggested.

In literature dealing with hydrogen thermodesorption from the rhodium surface considerable discrepancies in both temperature ranges and shares of individual forms of the desorbed hydrogen can be noted. Castner et al. (1, 2) found for Rh(111) and (331), that hydrogen desorbs up to about 250°C in the form of one peak. Yates et al. (3) observed two peaks in the spectrum of H$_2$ thermodesorption from Rh(111) up to about 150°C. Similar results for polycrystalline rhodium wire are presented by Mimeault and Hansen (4). Sosienkova et al. (5) found two or three peaks in the spectra of H$_2$ thermodesorption from Rh black and 5% Rh/BaSO$_4$ catalyst, respectively. A considerable part of hydrogen was desorbed in the range 350–600°C. Popova et al. (6) after activating 5% Rh/Al$_2$O$_3$ catalyst at 300°C obtained a thermodesorption spectrum reflecting three forms of H$_2$ and they ascribed the range 300–540°C to H$_2$ desorption from the support.

In analogous measurements for Rh black, hydrogen was desorbed within the range 0–210°C (6). After activating 5% Rh/TiO$_2$ catalyst with hydrogen at 400°C Apple et al. (7) distinguished three forms of H$_2$ in a thermodesorption spectrum with the maxima at 80, 240, and 540°C. Although the sources of the discrepancies in the above data may be numerous, particularly, in relation to high-temperature forms of H$_2$ desorption from rhodium, it can be noted that, except for Ref. (6), existence for these forms is conditioned by the presence of supports BaSO$_4$, Al$_2$O$_3$, TiO$_2$.

Wanke and Dougharty (8), using a HV apparatus, observed a monotonic decrease in successive titrations, H$_T$ and O$_T$, for 5% Rh/Al$_2$O$_3$ catalysts. According to them the cumulative effect of the formation of water in situ on the rhodium suggests that the decreasing uptakes result from interference with hydrogen adsorption by the water formed. In our previous paper (9), under conditions of pulsed gas chromatography, analogous effects were observed. However, these effects were ascribed to a blocking of that part of rhodium crystallites which was in the direct range of action of water (OH groups) adsorbed on Al$_2$O$_3$. This resulted not only in the decrease of hydrogen adsorption but oxygen adsorption as well. The decrease in H$_T$ and O$_T$ results has been confirmed recently by Fuentes and Figueras (10).

The main aim of this paper is to attempt to find a correlation between the decreased values of H$_T$–O$_T$ titrations and expected changes in the spectra of H$_2$ thermodesorption from Rh/Al$_2$O$_3$ catalysts. The only end product of titration reaction, under conditions of the method used, is water (11, 12) formed in situ on the rhodium surface; our intention has been to show its effect on adsorptive–desorptive properties of H$_2$ for Rh/Al$_2$O$_3$ catalysts.

The experimental details are as follows: Measurements of hydrogen adsorption H$_c$,

titrations H_T and O_T, and hydrogen temperature-programmed desorption (TPD) were carried out in the apparatus for pulsed gas chromatography investigations (13). Argon of volume velocity 100 cm^3/min was used as a carrier gas. For its purification molecular sieves of 13 X type and catalysts Cu/Al_2O_3 working at 200°C and MnO/Al_2O_3 at 25°C were applied (13, 14). Oxygen and hydrogen prepared electrolytically and purified were introduced into a stream of argon in 0.5-cm^3 volumes. A catalyst sample (2–4 g) was placed in a Pyrex tube of diameter 1.5 cm and heated in TPD measurements at a rate of 25°C/min. Catalysts 1 and 5% Rh/ Al_2O_3 were prepared by impregnation of γ-Al_2O_3 with aqueous solutions of Rh-$Cl_3 \cdot 3H_2O$, dried at 105°C, and reduced at 600°C for 16 h. The support surface was 90 m^2/g (BET, argon). Water adsorption was carried out by time-regulated contact of a sample with a stream of argon and water vapor, prepared in a saturator. For investigations Rh black (about 0.15 m^2/g Rh) and a mechanical mixture of 10% Rh black and 90% Al_2O_3 were also used. After many thermal pretreatments (H_2, Ar) the samples used for investigations revealed constant and reproducible adsorptive–desorptive properties.

Results of H_T and O_T titrations for a 5% Rh/Al_2O_3 catalyst, rhodium black, and a mechanical mixture of 25% Rh and 75% Al_2O_3, as a function of successive measurement cycles, are presented in Fig. 1. Besides, for 5% Rh/Al_2O_3 catalyst a curve representing H_T/O_T ratios is given. Figure 1 suggests that, in fact, only for supported catalysts Rh/Al_2O_3 a monotonic decrease in H_T and O_T values is observed. Further increase in the number of measurement cycles resulted in a decrease of the H_T/O_T ratio from 2 to about 1.8. At this stage, a considerable decrease in the share of fast and irreversible hydrogen adsorption was observed, whereas the character of the O_T titration process remained unchanged. When the same measurement procedure was employed it led, eventually, to almost
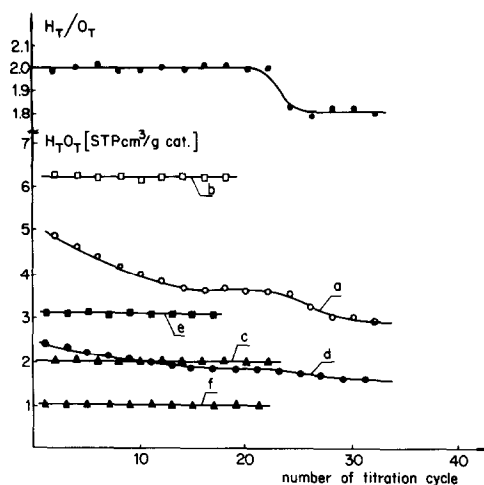

FIG. 1. Results of hydrogen and oxygen titration as a function of measurement cycles. Curves: a, b, c—H_T; d, e, f—O_T; a, d—for 5% Rh/Al_2O_3 catalyst; b, e—for Rh black; c, f—for mixture of 25% Rh and 75% Al_2O_3.

complete inhibition of titration processes. Only much prolonged time of contact of hydrogen with a sample (stream reduction) allowed increasing of O_T values. Repeated heating of the catalyst sample in a stream of the carrier gas or its reduction at an elevated temperature led to reproduction of the results presented in Fig. 1 (in Fig. 9). We suppose that the decrease in H_T–O_T results is caused by a blocking of a part of the rhodium surface by water (OH groups) adsorbed on Al_2O_3 in the direct vicinity of the metal. This, gradually increasing part of the rhodium surface would be inaccessible for successive titration reactions H_T–O_T. Further moisturizing of the catalyst sample, when the amount of water adsorbed on Al_2O_3 is comparable with the adsorptive capacity of the support, would result in prolonged presence of water on the rhodium surface. Water adsorbed on rhodium would form a kinetic-diffusive barrier for hydrogen adsorption. The absence of the effects of decreasing H_T and O_T values for Rh black and its mixture with Al_2O_3 (Fig. 1) may be due to the observed local exothermic effects of the reaction, which would prevent water adsorption both on the rhodium surface and in its direct vicinity on the

surface of alumina. A low degree of dispersion of the Rh black (about 0.15 m²/g Rh) may encourage local thermal effects of the titration reaction and on the other hand, limit the number of direct contacts of metal and alumina.

The influence of the number of titration cycles H_T–O_T on hydrogen thermodesorption for 1 and 5% Rh/Al_2O_3 catalysts is presented in Fig. 2. TPD spectra a and a' representing hydrogen desorption for a monolayer coverage (no water in the system) are characterized by the presence of three peaks of the maxima at about 120, 350, and 600°C. Apple et al. (7) presented a very similar spectrum of hydrogen TPD from 5% Rh/TiO_2 catalyst. A considerable shift of the temperature range of H_2 desorption toward higher temperatures, as compared with hydrogen TPD spectra presented by Yates et al. (3) for Rh(111), by Castner et al. (1, 2) for Rh(111) and (331), and by Mimeault and Hansen (4) for a polycrystalline rhodium wire, is probably due to the differences in pretreatment temperatures, and the presence of the support. Relatively low temperatures of pretreatment and reduction of the supported rhodium metallic phase together with the stabilizing effect of the support are sure to stimulate a relative increase in the number of high-energy hydrogen adsorption centers. As can be seen from Fig. 2 the increase in the number of H_T–O_T results in essential changes in quantitative participation of individual forms of the desorbed hydrogen and their temperature ranges.

Integration of TPD curves in Fig. 2 for 1% Rh/Al_2O_3 catalyst allowed determination of changes in the amount of desorbed hydrogen (Fig. 3). Changes in t_{max} of the high-temperature peak are also presented in Fig. 3. To our surprise, with increasing number of titrations, instead of the expected monotonic decrease in the total amount of desorbed hydrogen, we observed first its increase and then its diminution (curve a). Figure 2 seems to suggest that changes in size and position of the high-temperature peak are the most characteristic. The temperature of the maximum of this peak decreases reaching finally about 350°C (curve c, Fig. 3), whereas the surface area of the peak initially increases and then decreases approaching values close to zero (curve b, Fig. 3).

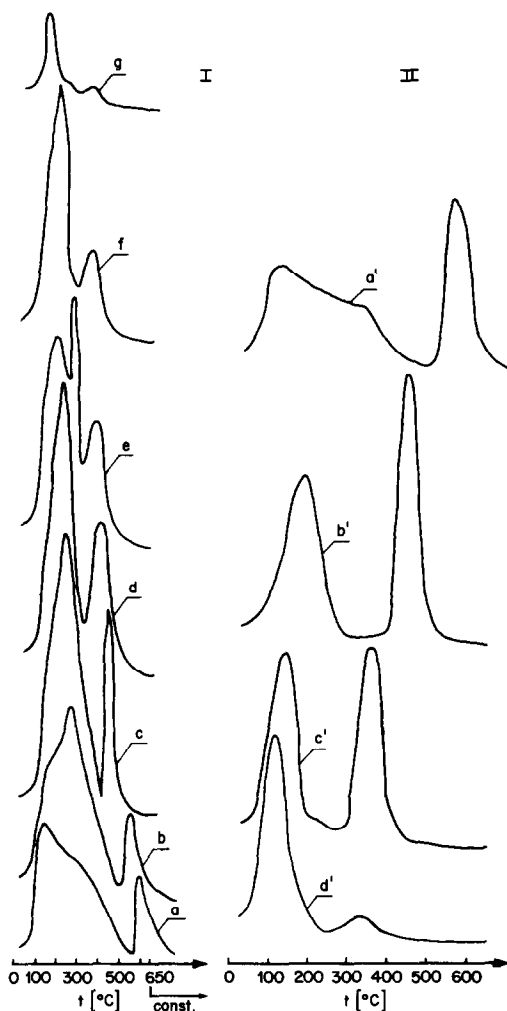The effect of small amounts of water formed on the rhodium surface on the spec-
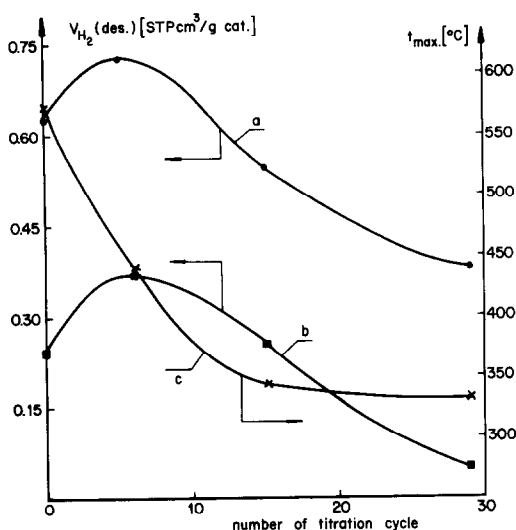

FIG. 2. Hydrogen thermodesorption from Rh/Al_2O_3 catalyst depending on the number of previously carried out titration cycles H_T–O_T; (I) 5% Rh; (II) 1% Rh. Curves: a, a'—after monolayer hydrogen adsorption; b, c, d, e, f—after 1, 3, 5, 10, and 15 titration cycles, respectively; g—adsorption with a stream of hydrogen (0.5 h) after previous saturation with a stream of argon and water vapor (16 h); b', c', d'—after 3, 10, and 15 titration cycles, respectively.

FIG. 3. Changes in the amount of desorbed hydrogen and the position of the high-temperature peak (t_{max}) depending on the number of titration cycles H_T–O_T for 1% Rh/Al_2O_3 catalyst. Curves: a—total desorption; b—high-temperature desorption; c—t_{max}.

tra of hydrogen TPD is shown in Figs. 4 and 5 for 1% Rh/Al_2O_3 catalyst. After oxygen adsorption, within the range of coverage from 0 to 1, hydrogen titration was carried out until hydrogen monolayer was obtained (Fig. 4) or the amount of hydrogen was so chosen as to obtain the degree of coverage $\theta_{H_2} \approx 0.31$ (Fig. 5). As can be seen, even small amounts of water formed in the system bring about considerable changes, especially in the high-temperature peak. Its size gradually increases with simultaneous shift of t_{max} toward lower temperatures. We did not find any influence of the number of H_T–O_T titrations on hydrogen thermodesorption from rhodium black, whereas a quite substantial effect was observed in the case of a mixture of Rh black and Al_2O_3 support. This is illustrated in Fig. 6. The character of changes in TPD spectra is analogous to that for Rh/Al_2O_3 catalysts.

In order to answer the question of whether the water introduced to the system from outside brings about effects analogous to those of the water formed *in situ* on the rhodium surface during titrations, a series of hydrogen TPD measurements was car-

ried out, the results of which are presented in Figs. 7 and 8. Before TPD measurements, a sample of 1% Rh/Al_2O_3 catalyst was treated with a mixture of hydrogen and water vapor for different periods of time and then rinsed with argon for 1 h (Fig. 7).

The sample of 5% Rh/Al_2O_3 catalyst was saturated with water vapor from the stream of argon for different periods of time, then hydrogen was adsorbed from the stream (1 h) and its excess was removed with argon for 1 h (Fig. 8). Comparison between the TPD spectra from Figs. 7 and 8 and those presented in Fig. 2 allows the conclusion, that water from outside has, in fact, an effect analogous to that of water formed on the surface of rhodium.

In order to determine the effect of pretreatment temperature on hydrogen TPD spectrum, a sample of 1% Rh/Al_2O_3 catalyst, previously wetted with a mixture of water vapor and argon at 25°C, was heated in the stream of argon at a given temperature (400, 450, 550°C) for 1 h. Then, after cooling it to room temperature, pulses of hydrogen were adsorbed until a monolayer
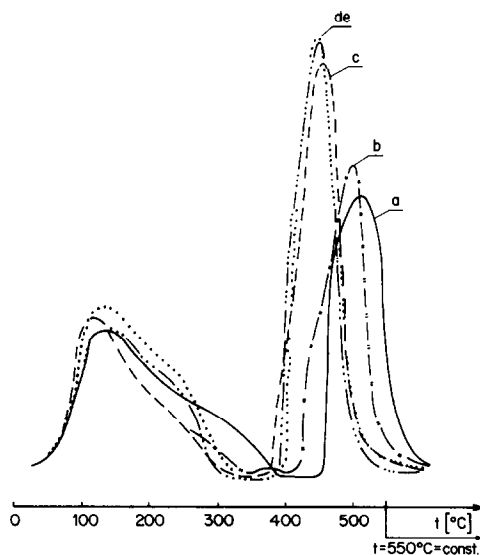

FIG. 4. Hydrogen thermodesorption from 1% Rh/Al_2O_3 catalyst after titration H_T–O_C. Degree of hydrogen coverage $\theta_{H_2} = 1$. Previous oxygen coverage θ_{O_2} was 0, 0.28, 0.56, 0.83, and 1, respectively, for curves a, b, c, d, and e.
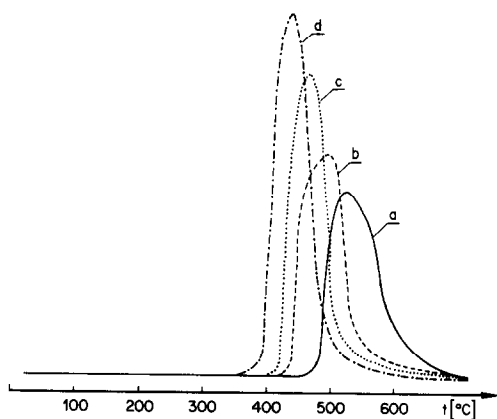
FIG. 5. Hydrogen thermodesorption from 1% Rh/ Al_2O_3 catalyst after titration H_T-O_C for a degree of hydrogen coverage $\theta_{H_2} = 0.31$. Previous oxygen coverage θ_{O_2} was 0, 0.28, 0.56, and 0.83, respectively, for curves a, b, c, and d.

FIG. 7. The influence of water from outside on hydrogen thermodesorption from 1% Rh/Al_2O_3 catalyst. Curves: a, b, c, d—adsorption with a stream of hydrogen and water vapor for 0, 0.25, 0.5, and 16 h, respectively.

coverage was obtained. The TPD spectra are presented in Fig. 9. Increased heating of the sample (and thus lower degree of wetting) results in a considerable shift of the high-temperature peak toward higher temperatures. In order to interpret the above-presented experimental material it is essential to consider the origin of hydrogen, especially its high-temperature form. Apple *et al.* (7), on the basis of NMR and TPD investigations of 5% Rh/TiO_2 catalyst, suggest that all the desorption peaks correspond to rhodium-bound species.

Taking into account the above-shown "sensitivity" of hydrogen TPD spectra for Rh/Al_2O_3 catalysts in relation to the number of titration cycles (the amount of water
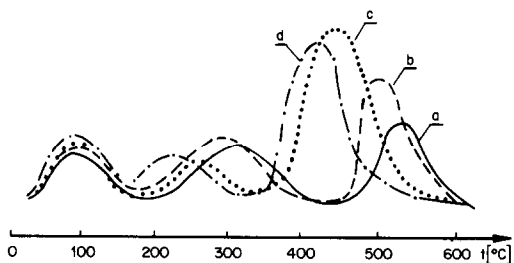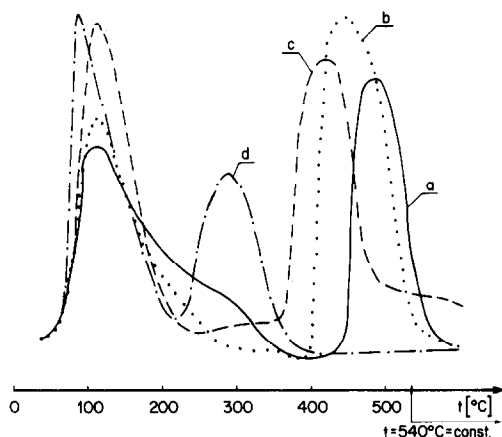

FIG. 6. Hydrogen thermodesorption from a mixture of 25% Rh + 75% Al_2O_3 after titrations H_T-O_T. Curves: a—monolayer; b, c, and d—respectively, 5, 10, and 15 titration cycles.
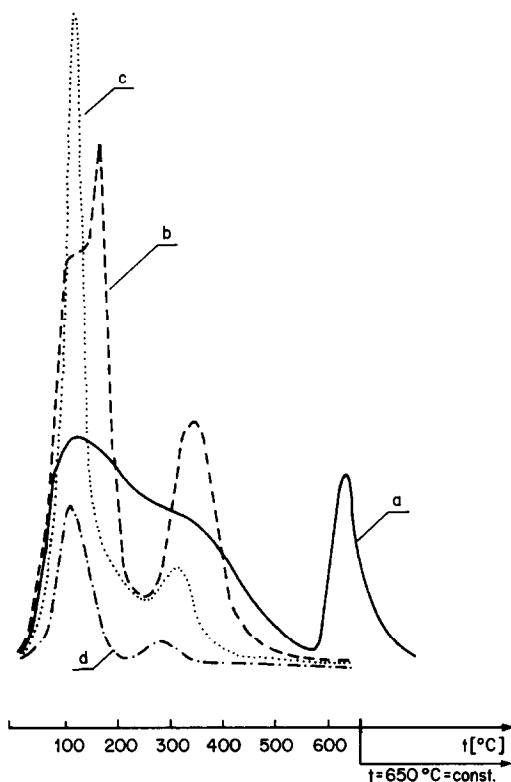

FIG. 8. The influence of water from outside on hydrogen thermodesorption from 5% Rh/Al_2O_3 catalyst. The sample was wetted using a mixture of argon and water vapor for different periods of time. Curves: a, b, c, d—0, 0.5, 1, and 16 h, respectively, and then the stream hydrogen adsorption was carried out for 1 h.

formed), oxygen–hydrogen interactions on the rhodium surface at room temperature should also be considered. The papers by Yates and co-workers (11, 12), Wanke and Dougharty (8), and also our earlier paper (9) allow the conclusion, that under conditions of the method used reduction of the surface oxidized sample is complete, and as a result, water desorbs onto a support and the metal surface is covered with a monolayer of hydrogen.

Accumulation of the inactive-toward-hydrogen form of oxygen in the surface layer of rhodium seems improbable. The existence of this form would disagree with the experimentally observed increase in the amount of desorbed hydrogen above the capacity of the monolayer. As follows from Fig. 3 the excess of hydrogen is about 20% of the monolayer.

The possibility of structural changes generating additional adsorptive centers in the surface layer of rhodium as a result of reduction of the adsorbed oxygen with hydrogen is considered in the paper by Amariglio and Amariglio (16) dealing with the role of oxygen in the reaction of ethylene hydrogenation at temperatures of about 200°C. Differences in temperature and inability to account for the effects observed in this paper

on the basis of the conception of structural sensitivity of the rhodium surface layer in H_T–O_T reaction, suggest the possibility of the existence of an additional source of hydrogen in the Rh/Al_2O_3 system. This source could be the support—Al_2O_3. The high-temperature peak of hydrogen TPD does not seem to correspond directly to the spillover effect of hydrogen taking into account that the high activation energy of diffusion of atomic hydrogen on the surface of Al_2O_3 at 400°C is 29 kcal/mole (15).

Kramer and Andre (15) reported the presence of a high-temperature peak of hydrogen TPD with a maximum at about 460°C for Ni and Pt/Al_2O_3 only after thermally activated (up to 400°C) hydrogen adsorption.

In our opinion the influence on hydrogen TPD of water from the surface of Rh/Al_2O_3 can be explained based on the synergetic effect of hydroxyl groups and hydrogen, adsorbed on the rhodium surface. The additional source of hydrogen would be OH groups of the support directly neighboring rhodium crystallites. The process of interaction of the support and the metal during hydrogen TPD can be schematically presented by the equation:

$$Rh_3 + \overline{H^+ \quad H} + O - \underset{|}{\overset{|}{Al}} - \xrightarrow{\text{temp}} H_2 + Rh_3 + O - \underset{|}{\overset{|}{Al}} - \tag{1}$$
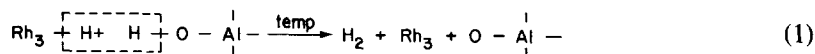
This equation would correspond to a high-temperature peak. The amount of additional hydrogen would increase with increasing concentration of OH groups. The shift of the high-temperature peak toward lower temperatures would be due to greater mobility of hydrogen atoms (protons), as the concentration of OH groups on Al_2O_3 increases.

If water were not introduced to the system the concentration of OH groups on Al_2O_3 would be limited by the conditions (temperature) of pretreatment and reduction of the catalyst (see Fig. 9).

Even at a temperature of about 1000°C

surface OH groups can be found on Al_2O_3 (17). Although in the literature there are no data concerning the so-formulated interaction between metal and support, in (18) McBride and Hall report that OH groups present on the surface of Al_2O_3 (originating from water vapor) are the source of hydrogen in the hydrogenation reaction of muconic acid to adipic acid, while heating Al_2O_3 to 400°C.

The possibility of surface reduction of Al_2O_3 is considered in (19). We assume that a part of the hydrogen atoms adsorbed on rhodium may be stabilized by directly neighboring OH groups of the support. This
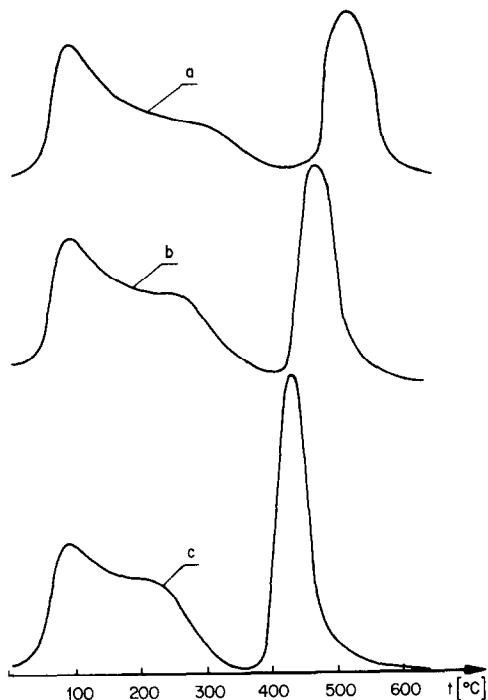
FIG. 9. The influence of reduction temperature on hydrogen thermodesorption of a sample of 1% Rh/ Al₂O₃ catalyst previously wetted. Reduction with a stream of hydrogen for 1 h. Curves: a, b, c—550, 500, and 420°C, respectively.

assumption would, at least partly, account for the differences in temperature ranges of hydrogen desorption from the surface of supported rhodium catalysts (this paper and (5–7)) as compared with that from un-supported ones (1–4).

With further moisturizing of the catalyst sample, adsorption of water directly on the metal would limit the possibility of hydrogen chemisorption conditioned both by kinetic-diffusive factors and dissociation of H₂ molecules. The absence of the effects of water influence on hydrogen TPD for Rh black confronted with clear effects for a mixture of Rh and Al₂O₃ (Fig. 6) confirms an essential role of the support. In spite of the fact that in this case the contact of rhodium and Al₂O₃ is limited, easy diffusion of hydrogen (protons) to the rhodium surface and its recombination are probable.

In conclusion, we would like to emphasize potential implications of the effects of water influence observed in this paper on adsorptive–desorptive properties of hydrogen for Rh/Al₂O₃ catalysts in relation to other systems of metal–hydrophilic support type, or catalytic reaction involving hydrogen, either as a reactant or as an impurity.

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