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Time Dependence of H_2 and O_2 Chemisorption on Rh/TiO_2 Catalysts

The reducibility of the support TiO_2 and the formation of surface defects by dehydration at high temperatures are important features in understanding the so-called strong metal-support interaction (SMSI) (*1–3*) of group VIII metals on TiO_2 after a high-temperature reduction. In the course of our studies (*4*), we noticed that support reduction is a relatively slow process and that, as a consequence, hydrogen chemisorption on a TiO_2 catalyst has a fast component, due to adsorption on the metal surface, and a slow component, due to spillover of H atoms from metal to support and subsequent support reduction. Oxygen chemisorption on reduced metals supported on TiO_2 shows a fast and slow component too. In this case the fast component can be attributed to chemisorption of O_2 on the metal surface and adsorption of O_2 on the partly reduced TiO_2, whereas the slow component is caused by further oxidation of the metal particles. In this note we present the main results of a study concerning the time dependence of H_2 chemisorption, as well as that of O_2 chemisorption, of an Rh supported on TiO_2 catalyst. The detailed results are published elsewhere (*5*).

The Rh/TiO_2 catalyst was prepared by pore volume impregnation of the support with an aqueous solution of $RhCl_3 \cdot 3H_2O$ (39 wt%, Drijfhout). The catalyst was made with 0.99 wt% Rh on the rutile modification of TiO_2 (Tioxide CLDD 1627/1, pore volume 0.57 ml g^{-1} and surface area 20 m^2 g^{-1}). Before use the support was washed twice with destilled water, dried at room temperature, and calcined at 500°C for 1 h to stabilize the surface area. After impregnation the catalyst was dried at room temperature for 24 h and subsequently for 10 h at 120°C.

Hydrogen and oxygen chemisorption measurements were performed in a conventional glass system at 22°C (*6*). Before a H_2 or O_2 chemisorption, the catalyst was reduced, or oxidized and reduced, at temperatures and during times to be specified. After evacuation (10^{-2} Pa) at the same temperature as the reduction temperature the cell was cooled down to room temperature and the chemisorption of H_2 or O_2 was started. For further details we refer to (*5*).

In Fig. 1 the hydrogen chemisorption results are presented by plotting the H/Rh ratios, calculated from the H_2 consumption and the total amount of Rh present, as a function of ln *t*. This was done because in that way nearly linear curves were obtained. The chemisorption measurements were performed after the following sequential treatments of the catalyst:

- Reduction for 1 h and evacuation for 1 h at 215°C of the impregnated and dried catalyst (Fig. 1A).
- A subsequent reduction for 2 h and evacuation for 1 h at 520°C, followed by a reoxidation at 140°C for 1 h, which is sufficient to break the SMSI state and reestablish normal chemisorption behavior (*6, 7*).
- After this treatment reductions and evacuations (for 1 h each) were carried out subsequently at 200, 300, 400, and 500°C, followed by H_2 chemisorption measurements. The results of these measurements are presented in Figs. 1B, C, D, and E, respectively.
- After the last measurement (Fig. 1E), the catalyst was further reduced at 500°C for 6 h, again an oxidation was applied at 140°C for 0.5 h, the catalyst was reduced for 1 h and subsequently evacuated for 1 h at 220°C, and then its H_2 chemisorption capacity was measured again (Fig. 1F). Further prolonged reduction at 220°C for 9 h, followed by evacuation at 205°C for 2 h, did not change the chemisorption behavior.

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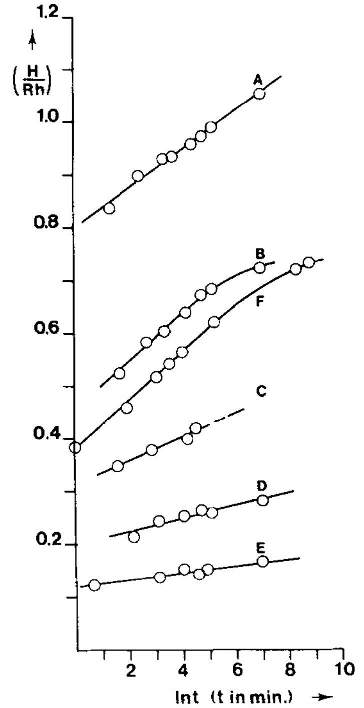

FIG. 1. Influence of reduction temperature on the time dependence of the H_2 adsorption of 0.99 wt% Rh/TiO_2. The H_2 chemisorption measurements were performed after the following sequential oxidation and/or reduction treatments of the catalyst: (A) reduction at 215°C of the impregnated catalyst, (B) reduction at 520°C followed by a reoxidation at 140°C and a reduction at 200°C, (C) reduction at 300°C, (D) reduction at 400°C, (E) reduction at 500°C, (F) reoxidation at 140°C and reduction at 200°C.

The resulting H/Rh vs ln t curve was equal to curve F.

All measurements show a linear relationship between H_2 chemisorption (expressed as H/Rh ratio) and ln t (especially in the first hours), a decrease in chemisorption with an increase in reduction and evacuation temperature, and a decrease in the slope of the H/Rh vs ln t curves with increasing treatment temperature. The results furthermore demonstrate that no equilibrium chemisorption was established within 18 h (ln t = 7) on this catalyst.

The decrease in H/Rh values between curves 1A and B demonstrates that the treatment at 520°C had caused sintering. Further treatment at intermediate temperatures followed by another treatment at 500°C did not induce further sintering, or only a little bit (cf. curves 1F and B). The decrease in H_2 chemisorption (cf. curves 1B to E) is therefore caused by SMSI only.

The time dependence of the chemisorption is not caused by a slow establishment of H_2 chemisorption at the Rh metal surface because, as previously published, no time dependence of hydrogen chemisorption was found on more conventional catalysts like Rh/SiO_2 and Rh/Al_2O_3 (*7*).

The only conclusion which can be drawn is that the slow uptake of H_2 by the catalyst is caused by the TiO_2 support. In addition to H_2 being bonded to the metal, H_2 must be bonded to the support. The time dependence of the H_2 chemisorption can be explained by considering the following metal catalyzed reduction process of the support, proposed by Huizinga and Prins (*4*):

$$2\ Ti^{4+} + 2\ O^{2-} + H_2 \overset{Rh}{\rightleftarrows} 2\ Ti^{3+} + 2\ OH^- \underset{T>200°C}{\rightleftarrows} 2\ Ti^{3+} + O^{2-} + H_2O\nearrow.$$

After reduction in H_2 at 200°C quite a bit of Ti^{4+} will be reduced by hydrogen atoms which have been spilled over from the rhodium metal particles to the support. The resulting protons are trapped as OH^- ions (see equation). The Ti^{3+} ions formed will be reoxidized during a subsequent evacuation at 200°C via the reverse reaction. As mentioned above, before a chemisorption measurement was performed the catalyst was reduced followed by an evacuation step at the same temperature. So, before hydrogen is admitted in order to determine the chemisorption capacity of the catalyst, the support was reoxidized completely after a pretreatment at 200°C. Hydrogen admission at room temperature then not only leads to a fast adsorption of H_2 on Rh, but also to slow spillover and reduction of Ti^{4+}. On the other hand, after reduction at high temperature (i.e., 500°C), Ti^{3+} will be formed and the surface of the support will be dehydrated. Therefore, during the following evacuation no reoxidation of the Ti^{3+} ions can take place. At the same time the rhodium has been changed into the SMSI state and therefore no H_2 chemisorption will take place at all. At intermediate reduction and evacuation temperatures there will be an intermediate behavior and as a result of this the H_2 chemisorption values will decrease with increasing treatment temperature and so will their time dependencies.

As, to the best of our knowledge, no information is available in literature whether there is a difference in O_2 chemisorption on a metal-on-TiO_2 catalyst in SMSI and normal state and whether the reduction temperature has any influence on this, we looked into the O_2 chemisorption capacity of the Rh/TiO_2 catalyst at room temperature. The measurements were performed after successive reductions and evacuations (1 h each) at temperatures of 200, 245, 280, 350, and 500°C. The results are presented in Figs. 2A, B, C, D, and E, respectively. To ensure that the starting conditions were the same in all cases, before each reduction–evacuation treatment and subsequent O_2 chemisorption experiment the catalyst was oxidized at 140°C for 0.5 h to bring the catalyst back from an eventual SMSI state to the normal state. Furthermore, to eliminate sintering effects the catalyst was prereduced at 500°C for 2 h and reoxidized at 140°C for 1 h.

The results demonstrate that just as for H_2 chemisorption, the O_2 chemisorption is dependent on time. In the first few hours there is a more or less linear relationship with ln *t*, thereafter the chemisorption levels off. The O_2 chemisorption (the fast component) is strongly dependent on the pretreatment too, increasing reduction–evacuation temperature leads to increasing O_2 chemisorption (cf. Figs. 2A to E). On the other hand, the slope of the curves (the slow component) is not much dependent on reduction temperature.

Measurements of the O_2 chemisorption of a reduced Rh/SiO_2 catalyst showed that this catalyst behaved similarly as the Rh/TiO_2 catalyst, with a very fast O_2 consumption, followed by a slow O_2 uptake which had a linear behavior with ln *t*. In contrast to the Rh/TiO_2 catalyst, however, the fast O_2 consumption of the Rh/SiO_2 catalyst proved to be independent of reduction temperature.

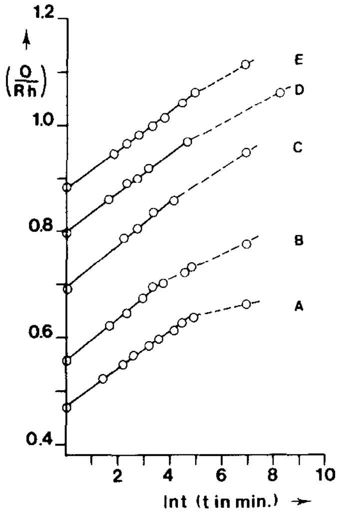

FIG. 2. Influence of reduction temperature on the time dependence of the O_2 adsorption of 0.99 wt% Rh/TiO_2. The O_2 chemisorption measurements were performed after successive reduction treatments at (A) 200, (B) 245, (C) 280, (D) 350, and (E) 500°C.

As the Rh/SiO_2 as well as the Rh/TiO_2 had ln *t* type O_2 chemisorptions, the slow chemisorption cannot be related to the support, but must be due to the oxidation process of the rhodium particles. Temperature-programmed oxidation (TPO) measurements on rhodium catalysts with quite similar dispersions as the Rh/TiO_2 catalyst under investigation demonstrated that chemisorption and further oxidation of the metal particles, which is a slow process, could be distinguished (*6*, *7*). So the slow O_2 chemisorption is attributed to the diffusion-limited further oxidation of the rhodium particles. In accordance with this explanation, the slope of the O/Rh–ln *t* curves is independent of reduction temperature. The catalyst had been pretreated at 500°C and any reduction at a lower temperature thus will not change the rhodium particle size, therefore the slopes stay constant.

Adsorption of O_2 on the Rh particles will contribute to the fast initial O_2 chemisorption, but there must also be a contribution from the TiO_2 support to explain the increase in O_2 chemisorption with increasing reduction temperature of the Rh/TiO_2 catalyst. When increasing the reduction temperature Ti^{3+} cations will be formed. Some of these cations will be reoxidized during the subsequent evacuation at the same temperature (the reverse reaction of the above equation), but at increasing temperature more and more of these cations will stay in the reduced form because of dehydration of the catalyst. As a consequence increasing numbers of Ti^{3+} ions can be oxidized during O_2 chemisorption. The major part of this reoxidation of Ti^{3+} ions by O_2 must be relatively fast, because otherwise the support reoxidation would have shown up in the slow O_2 chemisorption process in the form of increasing slopes at increasing reduction temperatures. This fast reoxidation is not in contrast with the observed slow reduction of the corresponding Ti^{4+} ions, considering that O_2 may directly chemisorb on Ti^{3+} because both O_2 and Ti^{3+} have radical character, while H_2 can only dissociatively adsorb on the metal and must be transported to the Ti^{4+} ions via an activated spillover process.

The results presented in this note clearly show that the room temperature adsorption of H_2 and O_2 on Rh on rutile TiO_2 catalysts exhibit a fast as well as a slow component. Similar results were obtained for Rh on anatase TiO_2 catalysts, too. It is clear that using H_2 chemisorption in order to determine the dispersion of metals supported on TiO_2 is delicate. In this respect we feel that our result of a slow H_2 spillover onto TiO_2 strongly suggests that a good method to separate H_2 adsorption on the metal from that on the support would be to extrapolate H_2 adsorption measurements to zero time, instead of to zero pressure.

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