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Characterization of Supported Cobalt and Cobalt–Rhodium Catalysts

II. Temperature-Programmed Reduction (TPR) and Oxidation (TPO) of Co/TiO_2 and $Co–Rh/TiO_2$

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The reduction–oxidation behavior of cobalt supported on titania has been studied by temperature-programmed reduction and oxidation (TPR and TPO). Cobalt, supported on titania, was rather easy to oxidize and subsequently hard to reduce. Because of this ease of oxidation, during passivation a considerable amount of cobalt was oxidized. The reduction of Co_3O_4 supported on TiO_2 proceeded in two stages, namely a primary reduction of Co_3O_4 to CoO and a subsequent reduction of CoO to Co. The addition of rhodium to cobalt caused the resulting bimetallic catalyst to be more difficult to oxidize, while the reducibility of the catalyst depended on the oxidation temperature. When oxidized below 800 K, the reduction proceeded at low temperatures, indicating that Rh_2O_3 was present in the surface of the bimetallic particles. To complete the oxidation, however, higher temperatures were needed and under these circumstances cobalt rhodate, $CoRh_2O_4$, was formed. The reduction behavior of a thoroughly oxidized catalyst revealed that only cobalt oxide was exposed, demonstrating that oxygen-induced surface enrichment of cobalt had occurred.

INTRODUCTION

Titania is one of the supports which exhibits a phenomenon called Strong Metal–Support Interaction, SMSI (*1*). Metal particles on such a support possess contradictory properties. The capacity of a titania-supported metal to adsorb hydrogen and carbon monoxide is diminished considerably after reducing the catalyst at temperatures above 773 K. In contrast, most metals active in Fischer–Tropsch synthesis reveal their highest activity when supported on carriers like TiO_2 (*2*). Although many explanations for SMSI have been put forward, no conclusive proof for any of them has yet been found.

In our laboratory we observed an increase in the activity in Fischer–Tropsch synthesis as well as in stability, when a $Co–Rh/TiO_2$ catalyst was reduced at higher temperatures prior to the synthesis (*3*).

In order to understand this phenomenon, insight into the reduction and oxidation behavior of the catalyst is a prerequisite. For that reason, we have used the techniques of Temperature-Programmed Reduction and Oxidation, TPR and TPO, respectively, to study the formation of alloys in bimetallic $Co–Rh/TiO_2$ catalysts. These techniques have proved to be sensitive tools in the investigation of the interactions between the metal atoms in bimetallic catalysts (*4–6*). In our first publication on Co–Rh catalysts, the behavior during reduction and oxidation of γ-Al_2O_3 supported Co–Rh catalysts has been discussed (*7*). The experiments presented in this paper were set up to test

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TABLE 1

Composition and Hydrogen Chemisorption Data for Titania-Supported Co, Rh, and Co–Rh Catalysts

Catalyst	wt% Co	wt% Rh	H/M 473[a]	H/M 773[b]
Co/TiO_2	2.01		0.14	0.06
Co/TiO_2	1.00		0.13	0.04
$Co-Rh/TiO_2$	1.19	1.72	0.19	0.09

[a] Based on hydrogen adsorption at room temperature after reduction at 473 K.

[b] Based on hydrogen adsorption at room temperature after reduction at 773 K.

and extend the model presented in that publication.

While TPR and TPO experiments of monometallic Rh/TiO_2 have been published (*8*, *9*), a comprehensive study of titania-supported cobalt has not been presented as yet. Therefore, before paying attention to the bimetallic $Co-Rh/TiO_2$ catalyst, the results of a TPR–TPO characterization study of Co/TiO_2 will be discussed.

EXPERIMENTAL

The TiO_2-supported Co and Co–Rh catalysts were prepared by incipient wetting of the TiO_2 support with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$. The support TiO_2 (anatase, Tioxide Ltd., CLDY 1367, surface area 20 $m^2 g^{-1}$, pore volume 0.6 ml g^{-1}) was (co)impregnated and then dried in air for 24 h at 393 K. Directly after drying, parts of the impregnated catalysts were reduced in flowing hydrogen by raising the temperature at 5 K min^{-1} and maintaining the final temperature, 773 K, for 1 h. After cooling to room temperature in flowing hydrogen, the catalysts, now in the metallic state, were passivated by replacing the hydrogen flow by a flow of nitrogen, and subsequently slowly adding oxygen up to 20%.

Atomic Absorption Spectroscopy (AAS) and colorimetry were used to determine the respective contents of Co and Rh in the dried catalysts. Table 1 presents the results of these analyses for the three supported catalysts to be discussed in this paper.

A conventional volumetric glass system was used to perform hydrogen chemisorption measurements. The passivated catalysts were reduced *in situ* in flowing hydrogen at 473 or 773 K for 1 h, followed by evacuation at 473 K for 1 h. Subsequently, hydrogen was admitted at the same temperature. After allowing the catalysts to cool to room temperature, hydrogen desorption isotherms were measured. The values of H/M presented in Table 1 are calculated by extrapolating the linear high-pressure part of the isotherms to zero pressure (see Ref. (*7*) for details). For both the monometallic and the bimetallic catalysts, hydrogen chemisorption is suppressed after reduction at 773 K. Note that in the case of the monometallic Co/TiO_2 catalyst reduced at 773 K, the presented H/M values are in the range of the experimental error. Adsorption of hydrogen on cobalt is known to be an activated process (*10*) and therefore particle sizes calculated from H/Co values may underestimate the true values. The mean diameter of the metal particles, calculated from H/M (cf. Table 1) for a 2 wt% Co/TiO_2 catalyst is about 9 nm (assuming hemisperical articles), while the mean diameter of the particles as determined by Transmission Electron Microscopy (TEM) is about 4 nm. Therefore, we cannot draw any conclusions from the results of these hydrogen chemisorption experiments on Co/TiO_2.

Ferromagnetic Resonance (FMR) spectra were measured directly after reduction, oxidation, and evacuation treatments, without exposing the sample to air, using a reactor designed by Konings *et al.* (*11*). The spectra were recorded at room temperature with a Varian E-15 X-band spectrometer. The position of the signals was calibrated with the aid of a Varian Strong Pitch sample ($g = 2.0028$, 3×10^{15} spins cm^{-1}). Because rotation of the sample made the spectra change (especially at low field) and relax slowly (within a minute), we feel that we are dealing with ferromagnetic, rather than superparamagnetic Co particles. We shall therefore refer to them as FMR spectra.

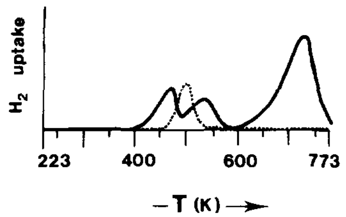

FIG. 1. Solid line: TPR profile of an impregnated and dried 2.01 wt% Co/TiO_2 catalyst; $H_2/M = 1.7$. Dotted line: TPR profile of a passivated 2.01 wt% Co/TiO_2 catalyst; $H_2/M = 0.66$.

Temperature-Programmed Reduction and Oxidation experiments were carried out in an apparatus similar to the one described by Boer *et al.* (*12*). The typical treatments during TPR and TPO have been discussed elsewhere (*8*, *9*). Since the metals are supported on titania, hydrogen chemisorption will be suppressed after reduction at higher temperatures. Thus, during cooling to 223 K after TPR, no hydrogen adsorption will occur, and as a consequence we did not need to perform an extra desorption before oxidizing the catalyst in a TPO experiment.

RESULTS AND DISCUSSION

1. Co/TiO_2

In Fig. 1 the hydrogen consumption, monitored as a function of the temperature during reduction, of an impregnated and dried Co/TiO_2 catalyst is shown (solid line). The total hydrogen consumption, expressed as molecules of hydrogen consumed per metal atom (H_2/M) amounted to 1.7. The reduction of divalent cobalt to zerovalent metallic cobalt requires only one hydrogen molecule per cobalt atom ($H_2/M = 1.00$) and the observed value of 1.7 is thus too high to account for the reduction of divalent or trivalent cobalt only. Bearing in mind, however, that the catalyst had been prepared using $Co(NO_3)_2 \cdot 6H_2O$, we must consider the reduction of NO_x groups as well. The peaks in the hydrogen consumption around 460 and 540 K are ascribed to the reduction of NO_x groups, since TPR measurements on unsupported CoO and Co_3O_4 demonstrated that cobalt oxides do not start to reduce before 573 K (*7*). The concurrent hydrogen uptake was quite low, in good agreement with the fact that at least part of the nitrate groups has desorbed from the catalyst during drying (as could be detected by the specific smell), as suggested by the equation

$$Co(NO_3)_2 \rightarrow CoO + 2NO_x$$

The last peak in the hydrogen consumption, around 700 K, resembles quite accurately the consumption peak during the reduction of unsupported CoO (*7*), suggesting that we are dealing with the reduction of CoO. The concurrent hydrogen uptake, $H_2/M = 1.1$, is in good agreement with this explanation, and suggests that the thermodynamically more stable Co_3O_4 phase has only been formed to a minor extent during drying. We thus conclude that the reduction of impregnated and dried $Co(NO_3)_2$ supported on TiO_2 proceeds via the reduction of residual NO_x groups, followed by the reduction of the remaining CoO (and partly Co_3O_4) particles, as suggested by the equations

$$Co(NO_3)_2 + 2H_2 \rightarrow CoO + 2H_2O + 2NO_x$$

$$CoO + H_2 \rightarrow Co + H_2O$$

$$Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O$$

After impregnation and drying, the catalyst was reduced. As the TPR of the impregnated and dried catalyst reveals, this reduction was complete at 773 K and the resulting catalyst is thus in the metallic state. After this direct reduction, the catalyst was passivated and stored for a few weeks. Figure 1 (dashed line) represents the hydrogen consumption during the TPR of this passivated 2 wt% Co/TiO_2 catalyst. The total hydrogen uptake amounted to 0.66, indicating that by passivation and storing about two-thirds of the cobalt particles had been oxidized to CoO, or alternatively, one-half of the particles to Co_3O_4. Since a transmission electron micrograph showed that the distribution was approxi-

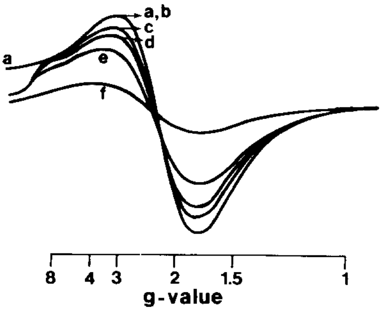

FIG. 2. FMR signal intensity as a function of time during passivation of a reduced 1.00 wt% Co/TiO_2 catalyst. (a) Reduced, (b) 5 min after exposure to air, (c) 45 min, (d) 75 min, (e) 180 min and (f) after several weeks.

mately symmetrical about a mean diameter of 4 nm, the hydrogen uptake is too high to account only for the reduction of surface CoO or Co_3O_4. Apparently, during passivation at room temperature, corrosive chemisorption of oxygen had occurred. Elegant proof for this was provided by FMR measurements. The FMR signal intensity of a ferromagnetic particle, such as a metallic cobalt particle on support, is proportional to the square of the number of constituent ferromagnetic atoms ($I = N^2$). Since N is proportional to R^3, where R is the radius of the particle, I is proportional to R^6. In Fig. 2, curve a represents the FMR spectrum of a 1 wt% Co/TiO_2 catalyst, under helium atmosphere, directly after reduction. After this spectrum had been recorded, air was admitted to the catalyst, and the FMR signal was monitored as a function of time. Figures 2b–f inclusive represent the FMR spectra recorded after exposure to air for several minutes, up to several weeks. Since the intensity of the last recorded signal was about 20% of the intensity of the reduced sample, we calculate that on average 45% ($= 0.20^{0.5} \times 100\%$) of the cobalt atoms were still in the metallic state and that 55% had been oxidized. On the assumption that the mean diameter of the cobalt particles is 4 nm, as measured by TEM, we calculate that about 33% of the cobalt atoms is present in the surface of the particles. This indicates that more than one layer of cobalt atoms had been oxidized and thus that corrosive chemisorption of oxygen had occurred. The radius of the remaining ferromagnetic, metallic kernel is about 75% of the radius of the original cobalt particle.

Temperature-Programmed Oxidation of a reduced catalyst also indicates that at room temperature corrosive chemisorption of oxygen has taken place. Figure 3 presents the oxygen uptake during a TPO of a reduced 2 wt% Co/TiO_2 catalyst. As follows from oxygen consumption during the switch peak, adsorption of oxygen started at the lowest temperature of the experiment, 223 K. The rate of oxygen uptake demonstrates that oxidation already took place around room temperature. Remembering that TPO was carried out at a heating rate of 5 K min^{-1} and passivation was carried out for a few weeks, TPO is not in disagreement with the conclusion reached from TPR of a passivated sample that during passivation a considerable amount of cobalt atoms was oxidized to CoO by corrosive chemisorption. Note that during TPO the total oxygen uptake, $O_2/M = 0.69$, is, within the experimental error, in good agreement with the value of 0.667 expected for oxidation to Co_3O_4.

Figure 4a presents the hydrogen consumption during TPR of the 2 wt% catalyst, after oxidation in TPO up to 773 K. We found that this reduction profile was only slightly dependent on the catalyst metal loading between 0.5 and 8 wt%. Two clearly separated peaks can be observed, indicating that the reduction of Co_3O_4 proceeds in two stages. We suggest that during the first stage Co_3O_4 is reduced to CoO:

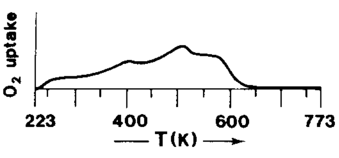

FIG. 3. TPO of a reduced 2.01 wt% Co/TiO_2 catalyst; $O_2/M = 0.69$.

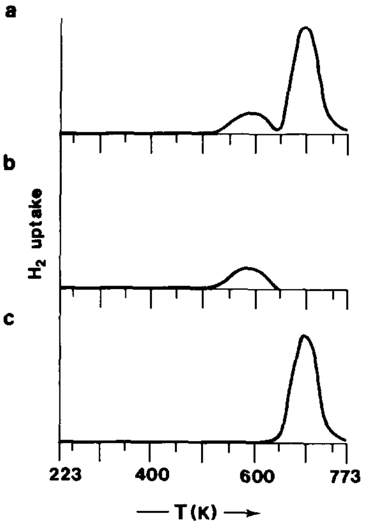

FIG. 4. TPR profiles of oxidized 2.01 wt% Co/TiO_2 catalysts. (a) "Complete" TPR profile, $H_2/M = 1.33$; (b) TPR up to 640 K, $H_2/M = 0.31$; and (c) TPR of the partly reduced (b) catalyst, $H_2/M = 1.02$.

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \quad (H_2/M = 0.33)$$

and that in the second stage CoO is reduced to metallic Co:

$$CoO + H_2 \rightarrow Co + H_2O \quad (H_2/M = 1.00)$$

The consumption of hydrogen during the two peaks, 0.31 and 1.02, is in satisfactory agreement with this explanation. Further proof is obtained from the following experiments. The catalyst, oxidized in a TPO up to 773 K, was reduced in a TPR up to 640 K, at which temperature the hydrogen uptake reaches a minimum (cf. Fig. 4a). At this temperature the catalyst was flushed with argon and cooled to 223 K. Subsequently, a second TPR was started, this time as usual up to 773 K. In Figs. 4b and c, these two TPR profiles are presented. The hydrogen consumption during the second TPR (Fig. 4c), matches exactly that of the last hydrogen consumption peak in a complete TPR (Fig. 4a). It is well known that many metals can adsorb and dissociate hydrogen, and thus can catalyze the reduction of an oxide, thereby lowering the reduction temperature. Such a shift toward lower temperatures is apparent from the reduction of CoO in the passivated and fully oxidized cobalt catalyst (cf. Figs. 1 and 4a) and in TPR results of other metals. Since we did not observe a shift in reduction temperature in the second TPR we can draw the conclusion that during the first, incomplete reduction (Fig. 4b) no metallic cobalt had been formed.

Again, FMR proved to be a useful technique to verify this. The FMR signal intensity of the sample reduced in TPR to 640 K was very small indeed compared with the signal intensity of a metallic Co catalyst and we calculated that the amount of metal formed was less than 4%. Thus, during the first TPR peak, no metal had been formed. Since the hydrogen consumption during this first reduction amounted to 0.31, it can be concluded that during this first reduction all Co_3O_4 has been reduced to CoO. CoO in its turn has been reduced in a second step to metallic Co.

In order to obtain more information on the oxidation of cobalt supported on TiO_2, we recorded a series of TPR profiles, presented in Fig. 5. Prior to each reduction, the catalyst had been oxidized in a TPO up to various temperatures, at which the sample was flushed with helium and cooled to 223 K. The numbers to the right of each profile represent the hydrogen uptake during reduction. After oxidation in TPO up to 423 K, the reduction profile as well as the hydrogen uptake, matches the reduction profile of the passivated sample within the experimental error. Note that after passivation the sample had been stored in air for several weeks. After oxidation up to 473 K the maximum in hydrogen consumption had shifted to 555 K and the total hydrogen uptake increased to 0.84. This value ($H_2/M < 1$), indicates that, as after passivation, the particles still had a metallic kernel. Obviously, this metallic kernel assisted the reduction of the oxide layer, since pure CoO is reduced only at temperatures above 650 K. Oxidation up to 523 K gave rise to the

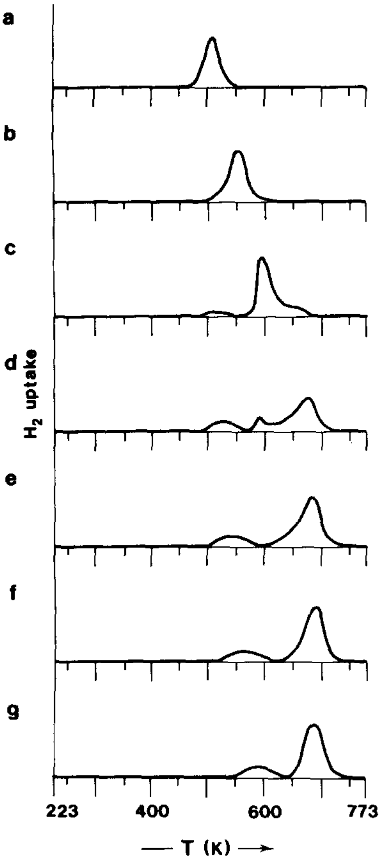

FIG. 5. TPR profiles of 2.01 wt% Co/TiO$_2$ catalysts oxidized at (H$_2$/M in brackets): (a) 423 K [0.67], (b) 473 K [0.84], (c) 523 K [1.10], (d) 573 K [1.19], (e) 623 K [1.24], (f) 673 K [1.28], and (g) 773 K [1.33].

reduction profile presented in Fig. 5c. Hydrogen uptake amounted to 1.10, indicating that in addition to CoO, Co$_3$O$_4$ had been formed. We attribute the main peak at 593 K to metal-assisted reduction of CoO. This metal assistance might be due to an increased number of oxygen vacancies at the surface, due to the presence of underlying metal atoms. The small peak around 518 K and the shoulder around 650 K are ascribed to the two-stage reduction of Co$_3$O$_4$. After oxidation up to 573 K, the metal-assisted reduction peak around 600 K had hardly shifted, but had decreased considerably in intensity. In contrast, the hydrogen uptake ascribed to the two-stage reduction of Co$_3$O$_4$ had increased in intensity. Oxidation at temperatures above 600 K did not change the situation significantly. During TPO no oxygen uptake occurred at temperatures above 600 K, indicating that oxidation was complete at 600 K. Both hydrogen and oxygen uptake indicate that the cobalt particles are completely oxidized to Co$_3$O$_4$, which is reduced in two stages, as discussed above.

Based on these findings, we propose the following model to explain the behavior of Co supported on TiO$_2$ during oxidation and reduction (see Fig. 6). After oxidation at mild temperatures, up to 500 K, corrosive chemisorption has taken place and thus the particles are partly oxidized, probably to CoO, as suggested by the fact that reduction of these particles proceeds in one step. The partly oxidized particles have a metallic kernel, giving rise to metal-assisted reduction. With increasing oxidation temper-

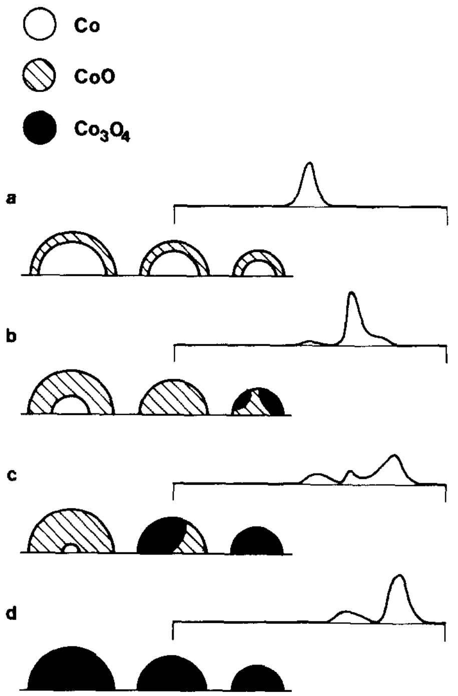

FIG. 6. Model for the different stages during oxidation of Co/TiO$_2$ catalysts. The associated TPR profiles are presented as well. (a) After passivation or oxidation at mild temperatures (up to 500 K), (b, c) after oxidation at temperatures between 500 and 600 K, (d) after complete oxidation (above 600 K).

ature, the oxidic skin becomes thicker and thus hampers metal-assisted reduction: the maximum in hydrogen uptake shifts to higher temperatures.

At oxidation temperatures between 500 and 600 K, the situation is slightly more complex. Hydrogen consumption indicates that Co_3O_4 had been formed, but one can also clearly observe hydrogen uptake due to metal-assisted reduction of CoO. We suggest that this is due to a distribution in cobalt particle size. After oxidation between 500 and 600 K only the larger particles have a metal kernel, while the smaller particles are completely oxidized. These small particles are made up of CoO and partly, depending on oxidation temperature and particle size, of Co_3O_4. This implies that Co_3O_4 will not be formed before the particle is completely oxidized to CoO. During reduction the Co_3O_4 phase of the latter particles will be reduced first, followed by metal-assisted reduction of the CoO particles having a metallic kernel. In the last stage the remaining CoO particles which do not have a metal kernel will be reduced. After a complete oxidation of the catalyst the TPR profile is characterized by the two peaks of the two-stage reduction of Co_3O_4. During oxidation at temperatures above 600 K no oxygen uptake occurs, indicating that oxidation is complete, while during subsequent reductions no significant changes in the two-stage reduction profile of Co_3O_4 is observed.

A somewhat different explanation might be to assume that under all conditions the thermodynamically most stable oxide Co_3O_4 had been formed. In that case the increasing H_2/Co values of the TPR experiments must be due to increasing thickness of the Co_3O_4 layer formed with increasing oxidation temperature. The low-temperature TPR peak observed after a low-temperature oxidation then has to be due to the reduction of this Co_3O_4 layer, and must be facilitated by the underlying metallic cobalt. The TPR peak between 520 and 600 K and the peak around 680 K obtained after a high-temperature oxidation are then assigned to the stepwise reduction of pure Co_3O_4 particles. There are, however, three difficulties with this explanation. The first is why Co_3O_4 pure is reduced in two steps and Co_3O_4 on top of metallic Co in a single step. The second problem is why the two peaks of the reduction of pure Co_3O_4 particles shift to higher temperature with increasing oxidation temperature. A third and more fundamental objection against the explanation in which under all circumstances Co_3O_4 is assumed to be present, is that Co_3O_4 can be present even though it is in contact with metallic Co. This seems very illogical. The argument that Co_3O_4 is more stable than CoO is certainly valid under thermodynamic equilibrium conditions. The oxidation of metals, however, is kinetically rather than thermodynamically controlled. This is immediately clear from our H_2/Co TPR data (Fig. 5), which demonstrate that apart from a metal phase one or two metal oxides are present in oxygen atmosphere at a certain pressure over a range of temperatures. This is against the phase rule ($F = C - P + 2$), since in the case of two components (Co and O) and three phases (Co, CoO_x, and O_2) there is only one degree of freedom (thus at a chosen O_2 pressure, temperature should have been fixed). For these reasons we prefer the interpretation that CoO is present in contact with Co at low oxidation temperatures.

2. *Co–Rh/TiO$_2$*

In Fig. 7a, the results of temperature-programmed reduction experiments of Co–Rh/TiO_2, after impregnating and drying, are presented. For comparison also the TPR results of Co/TiO_2 and Rh/TiO_2 are presented (Figs. 7b and 1). The reduction of the Co/TiO_2 catalyst has been discussed in the previous section. The hydrogen uptake in the temperature range of 373 to 473 K of the impregnated and dried $RhCl_3/TiO_2$ catalyst is ascribed to the reduction of $RhCl_3$ (*13*). The smaller peak in the hydrogen uptake around 323 K is most probably due to

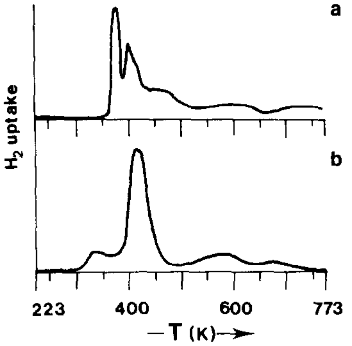

FIG. 7. TPR profiles of impregnated and dried TiO_2-supported catalysts. (a) Co–Rh, 1.19 wt% Co, 1.72 wt% Rh, $H_2/M = 1.50$; (b) Rh, 3.20 wt%, $H_2M = 1.70$.

the reduction of Rh_2O_3, formed by hydrolysis of $RhCl_3$ during impregnation and drying. The measured total hydrogen uptake, $H_2/M = 1.7$, exceeds the value expected for the reduction of trivalent to zero-valent rhodium, $H_2/M = 1.5$, because of metal-assisted reduction of the support visible at temperatures above 500 K (9).

The reduction of the impregnated bimetallic catalyst takes place mainly in the temperature range from 350 to 500 K, while the hydrogen uptake at temperatures above 500 K is again attributed to metal-assisted reduction of the support. Note that at temperatures above 600 K (where CoO, which resulted from the reduction of $Co(NO_3)_2$, is reduced), no other hydrogen uptake is visible, which indicates that $Co(NO_3)_2$ had been reduced below 600 K. Since trivalent rhodium, either present as Rh_2O_3 or $RhCl_3$, is reduced below 473 K, it is evident that rhodium-assisted reduction of $Co(NO_3)_2$ or CoO has occurred, and that both metal salts were close together after impregnation. The extent to which mixed salt particles were present is a question that is still under study. The hydrogen uptake, $H/M = 1.5$, indicates that all rhodium and cobalt is reduced in the TPR. The overconsumption $(1.5 - 1.23 = 0.27)$ is again ascribed to the reduction of nitrate groups and support. The fact that complete reduction of cobalt and rhodium occurs at temperatures where monometallic rhodium reduces, suggests either that (if hydrogen spillover is slow) bimetallic particles are formed, or that separate monometallic particles are formed when hydrogen spillover is fast. If the metal salts are mixed before reduction, bimetallic particles will be formed independently of the extent of hydrogen spillover. To study this in more detail, TPO and subsequent TPR profiles of the bimetallic Co–Rh and of the monometallic reference catalysts have been measured. In Fig. 8 the oxygen uptake as a function of temperature during oxidation of $Co-Rh/TiO_2$ and Rh/TiO_2 is presented (compare also the TPO of Co/TiO_2 in Fig. 3).

The behavior during oxidation of the monometallic Co/TiO_2 catalyst has been discussed in the previous section. Rhodium supported on titania was much harder to oxidize than cobalt. At temperatures above 600 K, where cobalt was completely oxidized, the oxidation of rhodium was still incomplete and continued until temperatures around 950 K. The amount of oxygen consumed, $O_2/M = 0.76$, indicates that rhodium was completely oxidized to Rh_2O_3. The overconsumption due to support reduction in the TPR of the dried sample and the oxidized sample is 0.2 and 0.1 H_2/M, respectively. The oxygen consumption corrected for reoxidation of the support is then 0.7 and within the experimental uncertainty is equal to the theoretically expected value of 0.75. The fact that rhodium was more diffi-

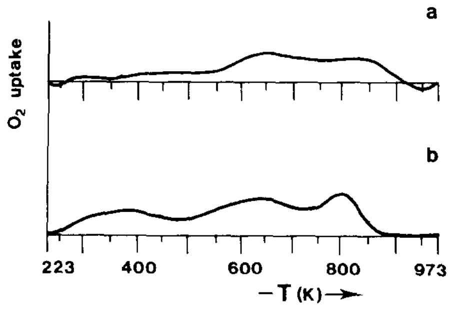

FIG. 8. TPO profiles of reduced TiO_2-supported catalysts. (a) Co–Rh, 1.19 wt% Co, 1.72 wt% Rh, $H_2/M = 0.56$; (b) Rh, 3.20 wt%, $H_2/Rh = 0.76$.

cult to oxidize than cobalt is surprising. The dispersion of rhodium on TiO_2 is better than that of cobalt and as TPO studies of Rh supported on TiO_2 and γ-Al_2O_3 have shown (*8, 9*), oxidation is more difficult for less well-dispersed metals. The conclusion must be that the thin layer of cobalt oxide formed on cobalt during TPO is less protective toward further oxidation than the corresponding layer of rhodium oxide on rhodium. This may well be related to a higher concentration of defects in cobalt oxide.

Oxidation of bimetallic Co–Rh/TiO_2 was even more difficult than oxidation of Rh/TiO_2. The total oxygen uptake, $O_2/M = 0.56$, is too low to account for complete oxidation of both metals to Rh_2O_3 and Co_3O_4. The measured value agrees much better with the value 0.61 expected for oxidation to Rh_2O_3 and CoO. This raises the question as to why cobalt was only partly oxidized in the Co–Rh/TiO_2 system, while in the monometallic catalysts Co was more easily oxidized to Co_3O_4 than Rh to Rh_2O_3. One of our findings in the previous section was that cobalt particles were not oxidized to Co_3O_4 as long as the particles had a metallic kernel. We assume that this also holds for bimetallic particles. Thus, as long as the Co–Rh particles contain a metallic kernel, cobalt in the outer layers is oxidized to CoO. In the meantime rhodium will be oxidized to the trivalent state. Trivalent rhodium preferentially occupies octahedral sites, while divalent cobalt occupies tetrahedral sites in oxides such as cobalt rhodate. Since both components, CoO and Rh_2O_3, are present in the particles, the formation of $CoRh_2O_4$ might proceed at relatively low temperatures. Since $CoRh_2O_4$ is quite stable, it is not unlikely that cobalt remains in the divalent state. After formation of the cobalt rhodate, however, an excess of cobalt is present. Based on the low oxygen uptake, we conclude that this excess of cobalt is oxidized to CoO.

Subsequent TPR experiments result in reduction profiles as presented in Fig. 9. As discussed before, the reduction of Co_3O_4 supported on TiO_2 did not start until 500 K and proceeded in two stages (cf. Fig. 5g). During the reduction of an oxidized Rh/TiO_2 (i.e., Rh_2O_3/TiO_2) catalyst, at least two peaks in the hydrogen uptake can be observed (Fig. 9b). The first and larger one around 325 K, is ascribed to the reduction of well-dispersed Rh_2O_3, while the second around 420 K, can be attributed to the reduction of larger, three-dimensional Rh_2O_3 particles (*9*). Hydrogen uptake at temperatures above 420 K can be ascribed, again, to the reduction of the support assisted by rhodium metal.

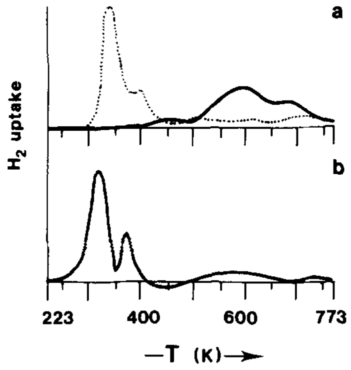

FIG. 9. TPR profiles of oxidized TiO_2-supported catalysts. (a) Co–Rh, 1.19 wt% Co, 1.72 wt% Rh, oxidized in TPO up to 773, $H_2/M = 1.04$ (dotted line), and 973 K, $H_2/M = 1.10$ (solid line); (b) Rh, 3.29 wt%, oxidized in TPO up to 773 K, $H_2/M = 1.60$.

As demonstrated in Fig. 9a, the final temperature during oxidation had a pronounced influence on the reducibility of the bimetallic particles. After oxidation in a TPO up to 773 K (at this temperature the oxidation was not complete) the reduction of the Co–Rh/TiO_2 catalyst took place in the same temperature range as that of oxidized Rh/TiO_2. Since no hydrogen uptake was visible below 300 K, we can exclude the possibility that rhodium metal was present in the oxidized bimetallic particles (*8, 9*). We thus conclude that in all particles Rh_2O_3 was present in the surface. In that case the rate of reduction of cobalt oxide in the bimetallic or monometallic particles will be enhanced, in the latter case by hydrogen spillover, as soon as rhodium oxide is reduced to rhodium metal.

After oxidation up to 973 K, the reducibility of the catalyst was drastically diminished. The fact that reduction proceeded at high temperatures suggests that no rhodium oxide was present in or near the surface of the particles, or in separate particles. Obviously, segregation had not occurred, thus providing evidence for a strong interaction between cobalt and rhodium oxide, probably resulting in the formation of $CoRh_2O_4$. The excess of cobalt is present as CoO and, since $CoRh_2O_4$ has a maximum in TPR around 510 K (*7*), CoO will most probably cover the $CoRh_2O_4$ particle. Therefore, reduction will not start until the surface layer of CoO starts to reduce. As can be seen from the monometallic Co/TiO_2 catalyst (cf. Fig. 9a(2) with Fig. 5c), this means that the particles will be reduced at rather high temperatures.

The present results for Co–Rh supported on TiO_2 fit well with the results obtained for Co–Rh supported on γ-Al_2O_3 (*7*) and with those obtained for Fe–Rh supported on SiO_2 (*14*). During reduction of the coimpregnated salts alloy particles are formed. When oxidized at elevated temperatures, the metals segregate, because the resulting metal oxides are immiscible. However, when Co–Rh supported on TiO_2 was oxidized at high temperatures we found indications that no segregation took place, but that cobalt rhodate, $CoRh_2O_4$, had been formed. That such a mixed oxide is not formed on γ-Al_2O_3 (*7*) must be due to the fact that cobalt oxide forms with alumina rather easily the $CoAl_2O_4$ spinel compound and thereby it diminishes its chances to form $CoRh_2O_4$.

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