

## Characterization of Supported Cobalt and Cobalt-Rhodium Catalysts

### III. Temperature-Programmed Reduction (TPR), Oxidation (TPO), and EXAFS of Co-Rh/SiO<sub>2</sub>

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Temperature-Programmed Reduction, Oxidation, and Extended X-Ray Absorption Fine Structure (TPR, TPO, and EXAFS) experiments supply clear evidence for the formation of bimetallic particles in Co-Rh/SiO<sub>2</sub> catalysts. After coimpregnation and drying, as well as after oxidation, the reduction of Co-Rh/SiO<sub>2</sub> catalysts proceeds at lower temperatures than the reduction of comparable Co/SiO<sub>2</sub> catalysts, indicating that rhodium catalyzes the reduction of the cobalt metal salt and cobalt oxide. EXAFS of the Rh K-edge of the Co-Rh/SiO<sub>2</sub> catalyst shows that after reduction the rhodium atoms in the catalyst have less cobalt neighbors than those in the Co-Rh alloy. The Rh-Co and Rh-Rh peak intensities in the Fourier transform of the Rh EXAFS were only slightly influenced by adsorption of oxygen at room temperature, whereas the EXAFS spectrum of the cobalt K-edge changed completely to that of cobalt oxide. From these results it is concluded that the reduced catalyst contains bimetallic Co-Rh particles, the interiors of which are enriched in rhodium, while the outer layers contain more cobalt. © 1986 Academic Press, Inc.

#### INTRODUCTION

TPR results obtained from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported bimetallic Co-Rh catalysts proved that after oxygen adsorption at room temperature the outer layer of the bimetallic particles contained mainly cobalt oxide, whereas in the particle core metallic rhodium was present (1). This does not necessarily mean that in reduced bimetallic Co-Rh particles the outer layer consists mainly of cobalt, since gas-induced surface enrichment of cobalt during oxygen admission may have occurred (2). On the other hand, cobalt enrichment in the surface of a reduced bimetallic Co-Rh particle is predicted on the basis of the difference in surface energy of cobalt and rhodium (3, 4), although experimental evidence for such an enrichment has not yet been presented.

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Studies published by Sinfelt and co-workers (5-8) have shown the usefulness of EXAFS in obtaining structural information on reduced bimetallic Ru-Cu, Os-Cu, Pt-Ir, and Ir-Rh catalysts. The first two systems are composed of a Group VIII and a Group IB metal, whereas the last two consist of elements from Group VIII only. The Ir-Rh system resembles the Co-Rh system best, since all three elements (Co, Rh, and Ir) have comparable electronic structures. From EXAFS data obtained on Ir-Rh (1 wt% Ir, 0.5 wt% Rh) supported on SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> it was concluded that the rhodium concentration in the surface region of the Ir-Rh particles was higher than in the interior (8).

In this publication we present the results of a characterization study of the Co-Rh/SiO<sub>2</sub> system by using TPR, TPO, and EXAFS on both the Rh and Co K-edges. SiO<sub>2</sub> was used as support because it does not exhibit the disadvantages of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> with respect to EXAFS. When  $\gamma$ -

Al<sub>2</sub>O<sub>3</sub> is used as a support, besides bimetallic Co-Rh particles, CoAl<sub>2</sub>O<sub>4</sub> is formed, and the EXAFS of the Co K-edge will then be composed of many different absorber-scatterer pairs, e.g., Co-Co, Co-Rh, Co-Al, and Co-O, which makes analysis of the signal difficult. TiO<sub>2</sub> is less suitable as support, since its absorption of the incident X-ray beam in the energy range of the Co K-edge is too high to obtain a proper EXAFS signal, when using ionization chambers as X-ray detectors. Another reason for using SiO<sub>2</sub> as a support is to test and extend the model developed for the formation of bimetallic Co-Rh particles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in previous publications (1, 9). Since a complete analysis of the spectra is still under study, the EXAFS results will be discussed qualitatively. However, as will become clear, the present EXAFS results already supply very useful information about the structure of the reduced bimetallic Co-Rh particles supported on SiO<sub>2</sub>.

#### EXPERIMENTAL

Three silica-supported catalysts were prepared: Rh/SiO<sub>2</sub> (3.9 wt% Rh), Co/SiO<sub>2</sub> (4.1 wt% Co), and Co-Rh/SiO<sub>2</sub> (4.9 wt% metal, atomic ratio Co:Rh = 1:1). The metal salts were deposited on the SiO<sub>2</sub> support (Grace, S. D. 2-324.382, 290 m<sup>2</sup> g<sup>-1</sup>) by incipient wetting with aqueous solutions of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Merck P.A.), RhCl<sub>3</sub> · 3H<sub>2</sub>O (Drijfhout), and of mixed solutions. The resulting impregnated catalysts were dried overnight at room temperature, then for 60 h at 393 K to remove the majority of the adsorbed water. Part of the impregnated and dried Co-Rh/SiO<sub>2</sub> batch was directly reduced in flowing H<sub>2</sub> (Research Grade, Hoekloos) by heating at 5 K min<sup>-1</sup> to 773 K and maintaining that temperature for 1 h. Directly after reduction, the catalyst was passivated at room temperature by replacing the H<sub>2</sub> flow by N<sub>2</sub> and subsequently slowly adding O<sub>2</sub> up to 20%. The Co and Rh contents of the dried catalysts were determined by using atomic absorption and colorimetry, respectively.

Hydrogen chemisorption measurements were performed in a conventional glass system at 298 K. Before measuring the desorption isotherms, the impregnated and dried catalysts were reduced at 773 K (heating rate 5 K min<sup>-1</sup>) for 1 h under flowing hydrogen (purified by passing through a Pd diffusion cell), and evacuated (10<sup>-2</sup> Pa) for another hour, at 773 K for Rh/SiO<sub>2</sub> and at 573 K for Co/SiO<sub>2</sub> and Co-Rh/SiO<sub>2</sub>. The cobalt-containing catalysts were evacuated at lower temperatures in order to avoid formation of water by dehydroxylation of the support and thus to avoid reoxidation of cobalt (1).

TPR and TPO experiments were carried out with circa 200 mg catalyst in an apparatus as described by Boer *et al.* (10). The flow rate of gases through the reactor was 5 cm<sup>3</sup> min<sup>-1</sup> and the temperature was raised at 5 K min<sup>-1</sup> within the temperature range of 223 to 773 K. The following sequence of treatments in the TPR apparatus has been used. The sample was dried in Ar at 393 K for 1 h and subsequently cooled to 223 K, after which a TPR profile was recorded. Next H<sub>2</sub> was removed from the reactor at 773 K for Rh/SiO<sub>2</sub>, at 573 K for Co/SiO<sub>2</sub>, and Co-Rh/SiO<sub>2</sub> by He flushing, to avoid H<sub>2</sub> chemisorption on the catalyst during cooling. After cooling to 223 K in He a TPO profile was measured, followed by cooling to 223 K and flushing with Ar for 1 h. Finally, a second TPR was recorded. For further details on the experimental TPR and TPO procedures, see previous publications (1, 11).

The EXAFS experiments were performed on X-ray beam line I-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) with a ring energy of 3 GeV and ring currents between 40 and 80 mA. The samples used for the EXAFS experiments were pressed into thin self-supporting wafers and mounted in an EXAFS *in situ* cell (12). The EXAFS spectra were recorded at liquid-nitrogen temperature. Spectra of the Co and Rh K-edges of Co-Rh/SiO<sub>2</sub> were recorded (under 100 kPa H<sub>2</sub>) after the pas-

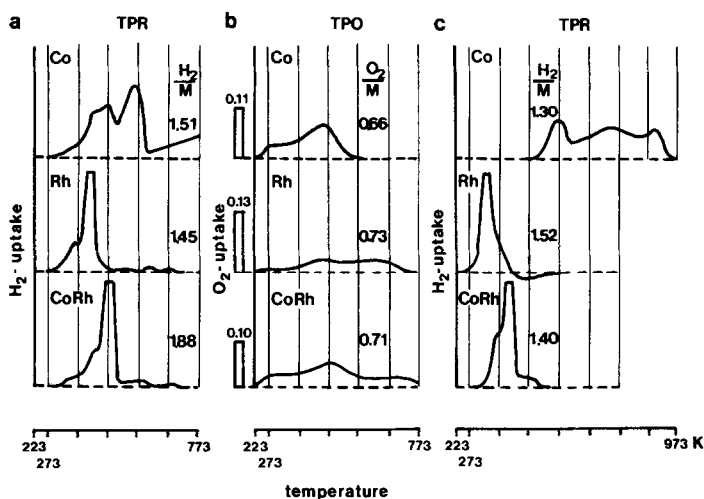


FIG. 1. TPR and TPO profiles of  $\text{SiO}_2$ -supported cobalt, rhodium, and cobalt-rhodium catalysts. The numbers next to the curves refer to the total  $\text{H}_2$  or  $\text{O}_2$  consumptions, expressed per total amount of metal atoms present in the catalysts. Temperature was increased with a rate of  $5 \text{ K min}^{-1}$ . Accuracies:  $\text{H}_2/\text{M}$ , 5%;  $\text{O}_2/\text{M}$ , 10%.

sivated catalyst had been reduced *in situ* at 673 K. After these measurements the sample was evacuated at room temperature and  $\text{O}_2$  was admitted. EXAFS spectra (under 100 kPa  $\text{O}_2$ ) were again recorded *in situ*. The Rh K-edge spectrum of the bulk Co-Rh alloy (atomic ratio Co:Rh = 1:1) has also been measured.

## RESULTS

The hydrogen chemisorption measurements yielded  $\text{H}/\text{M}$  (M counted as total number of metal atoms) values of 0.13, 0.44, and 0.25 for the reduced  $\text{SiO}_2$ -supported Co, Rh, and Co-Rh catalysts.

Profiles of TPR and TPO obtained with the silica-supported Co, Rh, and Co-Rh catalysts are shown in Fig. 1. The numbers printed next to the profiles correspond to the ratio of the amount of gas consumed and the total amount of metal.

Reduction of the impregnated and dried Co/ $\text{SiO}_2$  catalyst mainly occurs within the relatively broad temperature range of 273–600 K. However, at 773 K hydrogen uptake is still visible. The reduction of impregnated and dried Rh/ $\text{SiO}_2$  is already complete at 473 K. In the TPR profile two peaks

are visible, one at 368 K, which is assigned to the reduction of  $\text{Rh}_2\text{O}_3$  (formed by hydrolysis during impregnating and drying) and one at 413 K, at which temperature  $\text{RhCl}_3$  is reduced (13). The TPR profile of the impregnated and dried bimetallic catalyst shows that the reduction takes place mainly between 273 and 510 K. This demonstrates that the rate of reduction of cobalt nitrate is enhanced by the presence of rhodium and suggests, but does not prove, that both metal salts are in intimate contact with each other after impregnation. Such a proof should be obtained from an experiment subsequent to the TPR experiment. For the same reason as mentioned in our study of  $\gamma\text{-Al}_2\text{O}_3$ -supported cobalt catalysts (1), the observed  $\text{H}_2/\text{M}$  values for the nitrate-containing catalysts give no indication about the reduction degree of the metals after TPR; the simultaneous reduction of the residual nitrate groups gives rise to an enhanced  $\text{H}_2/\text{M}$  value. The total amount of hydrogen consumed during TPR of Rh/ $\text{SiO}_2$  indicates that the reduction of rhodium was complete ( $95 \pm 5\%$ ).

The TPO profiles of the reduced catalysts (Fig. 1) show oxygen uptake at 223 K due to

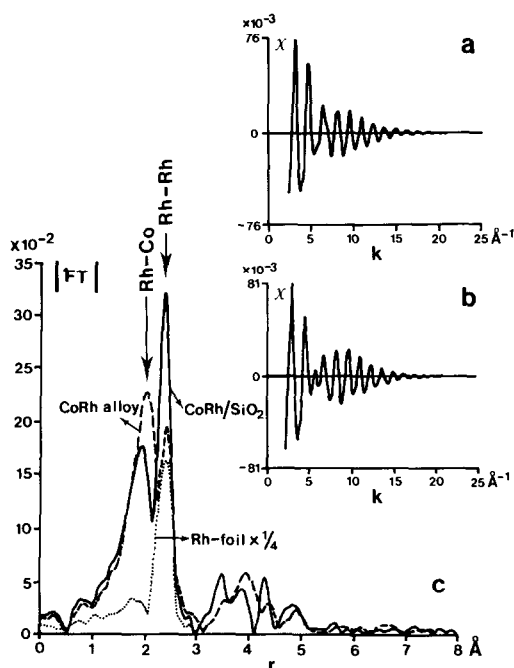


FIG. 2. EXAFS of the Rh K-edge of the Co-Rh alloy and the Co-Rh/SiO<sub>2</sub> catalyst. (a) Normalized EXAFS data for the Co-Rh alloy (molar Co/Rh ratio = 1); (b) Normalized EXAFS data for Co-Rh/SiO<sub>2</sub>, reduced *in situ* at 673 K; and (c) the  $k^1$  Fourier Transforms of the EXAFS of the Co-Rh alloy, the reduced Co-Rh/SiO<sub>2</sub> catalyst, and also, for  $r < 3$  Å, of the Rh foil.

chemisorption. The oxidation of Co supported on silica is already complete at 573 K, whereas higher temperatures are needed to completely oxidize the Rh and Co-Rh catalysts. This might seem somewhat surprising in the light of a finding that better-dispersed Rh catalysts are easier to oxidize (11). Apparently, the cobalt oxide layer formed during oxidation of Co catalysts is less protective toward further oxidation of the kernel than the Rh<sub>2</sub>O<sub>3</sub> layer of Rh catalysts. If it is assumed that during oxidation Co<sub>3</sub>O<sub>4</sub> and Rh<sub>2</sub>O<sub>3</sub> are formed, the reduction degrees of the metals after the first TPR, as determined from the observed O<sub>2</sub>/M values, are within the experimental uncertainty equal to 100%.

Subsequent TPR measurements resulted in profiles as presented in Fig. 1c. In order to reduce Co<sub>3</sub>O<sub>4</sub> completely, the TPR had

to be extended to 973 K. The TPR profile is characterized by hydrogen uptake in a wide temperature range. The reduction starts at 473 K and is complete at 973 K. The reduction of SiO<sub>2</sub>-supported Rh<sub>2</sub>O<sub>3</sub> is complete at 410 K; the concurrent hydrogen uptake is concentrated in a single peak with a maximum at 350 K. Above 420 K the hydrogen consumption is negative, because of hydrogen desorption from the catalyst surface. The reduction of the bimetallic catalyst is characterized by a main peak around 400 K and a shoulder at lower temperatures. The fact that an oxidic bimetallic Co-Rh catalyst is reduced at higher temperatures than an oxidic monometallic Rh catalyst can be explained by the difference in metal dispersion. As shown before (11), large rhodium oxide particles reduce at higher temperatures than smaller particles. Note that the reduction of the bimetallic catalyst is complete before the oxidized monometallic Co catalyst starts to reduce. This suggests that after oxidation the two metal oxides are close together. The observed H<sub>2</sub>/M values show that the reduction degrees of the three catalysts are high; within the experimental error they are equal to 100%.

In order to obtain more information about the structure of the metal particles in the reduced Co-Rh/SiO<sub>2</sub> catalyst, EXAFS spectra were measured. Figures 2a and b show the normalized EXAFS function  $\chi(k)$  of the Rh K-edge of, respectively, the Co-Rh alloy and the Co-Rh/SiO<sub>2</sub> catalyst, reduced *in situ* at 673 K. The oscillations are due to rhodium as well as cobalt neighbor atoms. The associated  $k^1$  Fourier Transforms (FT's) of the EXAFS functions, taken over the wavevector range of 3–15 Å<sup>-1</sup>, are presented in Fig. 2c. This figure also includes, for  $R < 3$  Å, the  $k^1$  Fourier Transform (reduced four times) of the EXAFS of Rh foil performed on a  $k$ -interval of 3–15 Å<sup>-1</sup> (14). Note that the peaks in the transformed functions are shifted from the true interatomic distances because of phase shifts (15). The FT's of the bimetallic systems are characterized by two peaks, one

around 2.4 Å, another around 1.9 Å. Since the main peak in the FT of the Rh foil K-edge is situated around 2.4 Å as well, we ascribe the first peak to rhodium nearest neighbors. The latter peak cannot be assigned to a side lobe, caused by the nonlinear  $k$ -dependences of the backscattering amplitude and the phase of rhodium, since the peak intensity is too high. As was proved by X-ray diffraction the metals cobalt and rhodium in the Co-Rh alloy are homogeneously mixed, and therefore, on the average, each rhodium atom is surrounded by six rhodium and six cobalt atoms and vice versa. Although a complete quantitative analysis of the EXAFS data must await further study, the results of a preliminary qualitative analysis prove beyond any doubt a difference in length of the Rh-Rh bond ( $2.66 \pm 0.02$  Å) and the Rh-Co bond ( $2.60 \pm 0.02$  Å). The peak around 1.9 Å is then caused by interference of Rh-Rh and Rh-Co EXAFS oscillations. The peak intensity is a measure for the total amount of Rh-Co bonds and therefore we denote this peak as the Rh-Co peak. The EXAFS spectrum thus proves that after reduction of the coimpregnated salts bimetallic (alloyed) Co-Rh particles are present, as was already suggested by the TPR results.

Figure 2c clearly shows that the intensity of the Rh-Co peak of the reduced Co-Rh/SiO<sub>2</sub> catalyst is smaller, and the intensity of the Rh-Rh peak is larger, than the intensity of the comparable peaks of the Co-Rh alloy. This indicates that the rhodium atoms in the reduced catalyst are more surrounded by rhodium atoms than by cobalt atoms.

In order to investigate the influence of oxygen on the structure of the bimetallic particles, EXAFS spectra were recorded after oxygen admission at room temperature to the reduced catalyst, leading to a passivated catalyst. The intensity of the Rh-Co and Rh-Rh peaks in the rhodium transform are only slightly influenced by adsorption of oxygen. On the other hand, the EXAFS spectrum of the Co-Rh/SiO<sub>2</sub>

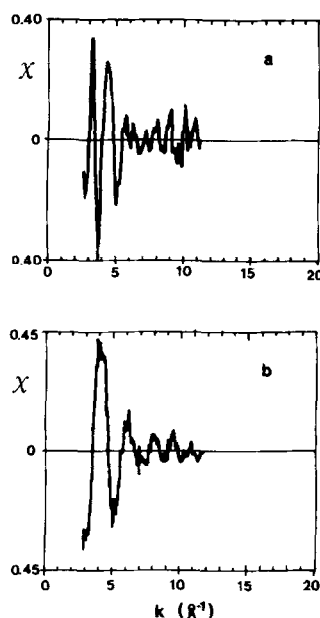


FIG. 3. Normalized EXAFS data of the Co K-edge of the Co-Rh catalyst: (a) reduced at 673 K; (b) subsequently exposed to air.

catalyst taken at the Co K-edge changes drastically after oxygen adsorption (Fig. 3). The much faster decrease of the EXAFS intensity with  $k$  demonstrates that after oxygen adsorption the average cobalt atom has low- $Z$  (oxygen) atoms as neighbors.

#### DISCUSSION

With regard to the formation of bimetallic Co-Rh particles on a support, the results of this investigation completely fit into the picture obtained for Co-Rh supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (cf. Fig. 4). A difference is that in the case of the SiO<sub>2</sub>-supported catalyst no irreducible compounds such as CoAl<sub>2</sub>O<sub>4</sub> are formed.

The TPR profiles of the impregnated and dried catalysts suggest that the two metal salts in Co-Rh/SiO<sub>2</sub> might be in intimate contact, because the Co-Rh/SiO<sub>2</sub> catalyst reduces at lower temperatures than the monometallic Co/SiO<sub>2</sub> catalyst. Once the more noble rhodium metal is formed, it catalyzes the reduction of the less noble cobalt metal salt. Real proof for the formation of

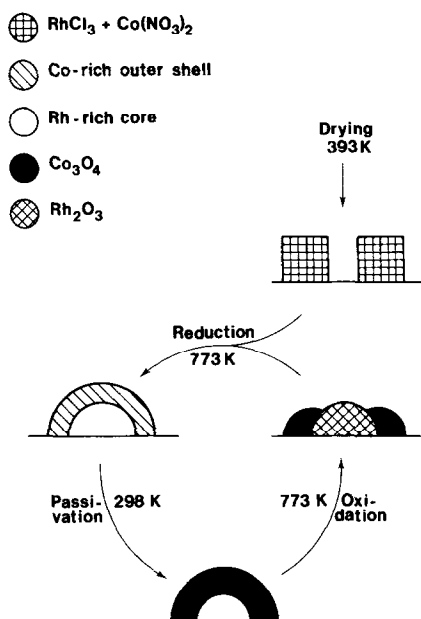


FIG. 4. Model for the formation of bimetallic Co–Rh particles during reduction of the impregnated catalyst and the change in structure of the particles during different treatments.

bimetallic particles comes from the EXAFS measurements. The Co–Rh phase diagram shows that the two metals form a homogeneous solid solution (16) and as a consequence, once an alloy is formed, there is no driving force to separate the metals during reduction.

Even without a detailed and lengthy analysis (for which spectra of reference compounds as well as spectra at different Co to Rh ratios would be needed), the Rh and Co EXAFS spectra as such contain (qualitative) information, which is very valuable in answering questions such as whether bimetallic (alloyed) Co–Rh particles have been formed and whether there is surface enrichment in such particles. The EXAFS spectra prove that bimetallic particles are indeed formed during reduction. The FT of the EXAFS function on the Rh K-edge of the Co–Rh/SiO<sub>2</sub> catalyst shows that after reduction of the catalyst a rhodium-rich phase is formed, since the rhodium atoms have more rhodium neighbors than in the

Co–Rh alloy. It is obvious that the formation of a phase, rich in rhodium, must be accompanied by the formation of a phase which is rich in cobalt. The bimetallic particles formed during reduction apparently consist of an inner part which is rich in rhodium, whereas the outer layer is enriched in cobalt, since: (i) the rhodium-rich phase is hardly affected by oxygen admission at room temperature (the EXAFS spectrum of the Rh K-edge is only slightly influenced); (ii) oxygen adsorption changes the coordination shell of cobalt completely and the EXAFS spectrum of the Co K-edge after O<sub>2</sub> admission (Fig. 3b) is characteristic for Co–O coordination.

Thus, in agreement with predictions based on the difference in surface energy for Co and Rh (3, 4), EXAFS has proved that during reduction of a Co–Rh catalyst cobalt enrichment in the surface of bimetallic particles takes place. Note that for an equiatomic alloy the contributions of heat of solution and of size mismatch are much less important than for a dilute alloy, although, in contrast to what Miedema has stated (4), they can never be disregarded. Abraham and Brundle (17) have predicted that a Co–Rh alloy will be enriched in rhodium. Their prediction applied to a cobalt-rich alloy, however, and furthermore, they used a theory, which according to Miedema (4) largely overestimates size mismatch and therefore predicts rhodium, instead of cobalt, enrichment of the surface.

Comparison of the TPO profiles for the three catalysts shows that the same high temperatures are needed for complete oxidation of the Rh/SiO<sub>2</sub> as for the Co–Rh/SiO<sub>2</sub> catalyst. During TPO the cobalt-rich surface is oxidized first, as proved by EXAFS, and therefore the oxygen consumption at higher temperatures is caused by oxidation of the rhodium-rich core. After oxidation cobalt and rhodium are present as Co<sub>3</sub>O<sub>4</sub> and Rh<sub>2</sub>O<sub>3</sub>.

The TPR profile of the oxidized Co/SiO<sub>2</sub> catalyst shows that a temperature of 973 K is needed to reduce the metal oxide,

whereas bulk  $\text{Co}_3\text{O}_4$  is reduced completely around 730 K. This result is in accordance with the findings of Paryjczak *et al.* (18) and was interpreted in terms of a metal-support interaction. Most probably some cobalt silicate is formed at the cobalt oxide-support interface, which is hard to reduce. If the reduction is performed at intermediate temperatures, cobalt oxide is reduced, but cobalt silicate resists reduction. This cobalt silicate serves as a "glue" attaching the metallic particle to the support.

We note that the reduction of the oxidized bimetallic particle occurs within the same temperature range as the reduction of the oxidized monometallic Rh/SiO<sub>2</sub> catalyst and is complete below the temperature at which the oxidized Co/SiO<sub>2</sub> catalyst starts to reduce. Apparently, rhodium catalyzes the reduction of cobalt oxide, which implies that both metal oxides are close together.

The general aspects of the TPR and TPO profiles of the Co, Rh, and Co-Rh catalysts do not depend much on the support. Of course, there are some differences, but these can easily be explained by such effects as dispersion (the TiO<sub>2</sub> we used had a much smaller surface area than the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), and interaction between support and cobalt ions (with Al<sub>2</sub>O<sub>3</sub> even part of the cobalt ions cannot be reduced at all, whereas cobalt ions on SiO<sub>2</sub> can only be reduced fully at high temperature). Special attention might be attracted by the fact that the formation of CoRh<sub>2</sub>O<sub>4</sub> was only indicated on TiO<sub>2</sub>. However, this seemingly different behavior of TiO<sub>2</sub>-supported Co-Rh might be rather trivial, because it was only on TiO<sub>2</sub> that we had to go to 900 K to be able to fully oxidize Rh and Co-Rh during TPO. The reason for this is not completely clear, but might be due to the fact that small TiO<sub>x</sub> species on top of the metal particles (being brought there when the metal compounds were being reduced and brought into the SMSI state) might have a negative influence on the rate of oxidation of the metal particles. Because of the fact that we went to 973 K during TPO only with

Co-Rh/TiO<sub>2</sub>, it is no surprise that only in this system was the formation of CoRh<sub>2</sub>O<sub>4</sub> inferred. Indeed, no CoRh<sub>2</sub>O<sub>4</sub> was formed when Co-Rh/TiO<sub>2</sub> was oxidized just to 773 K (cf. Fig. 9a of Ref. (9)), as in the cases for Co-Rh supported on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

Finally, we consider the implications of our observations for other bimetallic catalysts. The conceptual model of the structural changes which occur upon oxidation and reduction treatments (cf. Fig. 4) appears to be valid for Co-Rh supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1), TiO<sub>2</sub> (9), and on SiO<sub>2</sub>. This model may even be extended to other alloys because as long as they form solid solution they will show similar behavior. Examples are: Fe-Rh (19), Ni-Rh (20), Pt-Ru (21), Pt-Ir (22-25), Pt-Re (26), and Ru-Cu (27). Spectroscopic proof for the formation of bimetallic particles has been presented for two other catalysts which are closely related to Co-Rh/SiO<sub>2</sub>, namely Fe-Rh/SiO<sub>2</sub> and Ni-Rh/SiO<sub>2</sub>. For the Fe-Rh catalyst this was proved by a combination of Mössbauer, XPS, and TPR measurements (19), while for the Ni-Rh catalyst ferromagnetic resonance and TPR gave the proof (20). The fact that for the reduced Ni-Rh catalyst no FMR signal could be observed established beyond any doubt that only bimetallic, nonmagnetic particles had been formed.

Generally, during reduction of a coimpregnated bimetallic catalyst alloying of the two metals takes place. Once noble metal particles have been formed, they serve as catalysts in the reduction of the salt of the less noble metal. An intimate contact is not a necessary prerequisite to form bimetallic particles during reduction, as reported by Bond and Yide (27) for RuCl<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> supported on SiO<sub>2</sub>. Their TPR results showed that RuCl<sub>3</sub> was reduced first, so the proposed mechanism of cluster formation was that Cu(NO<sub>3</sub>)<sub>2</sub> was reduced by hydrogen spill-over from ruthenium and the resulting copper atoms then migrated to ruthenium particles.

The surface of bimetallic particles is en-

riched in the component which has the lowest surface energy, e.g., Co in Co-Rh, Fe in Fe-Rh, and Pt in Pt-Ru. A mild oxidation leads to surface enrichment of the metal which has the highest affinity toward oxygen. The bimetallic particles stay largely intact after oxygen adsorption at moderate temperatures, since although in the presence of adsorbed oxygen the clusters are thermodynamically unstable, the rate of segregation of metal oxides is slow. This has been found for Co-Rh, Pt-Ru, Fe-Rh, as well as Pt-Re. Generally, a thorough oxidation induces segregation of the metal oxides. Thus, the intimacy of the two metals in the reduced bimetallic catalyst is terminated by an oxidative treatment. Segregation depends on the miscibility characteristics of the bulk metal oxides and on the strength of the interactions between metal oxides and support. An example of a catalyst in which no segregation of the metal oxides takes place is Co-Rh supported on TiO<sub>2</sub>, probably due to the formation of CoRh<sub>2</sub>O<sub>4</sub> (9). A low-temperature reduction of an oxidized catalyst in which segregation has taken place may lead to a catalyst in which both metals are separated. This means that the specific advantages of alloying are lost. A high-temperature reduction, however, usually leads to co-clustering of the metals, but metal dispersion may be less compared with the catalyst before oxidation. Thus, Wang and Schmidt (28) observed that upon oxidation of a Pt-Rh/SiO<sub>2</sub> catalyst Rh<sub>2</sub>O<sub>3</sub> forms at the edge of Pt metal cores. Reduction at 298 K then produced separate Rh and Pt particles, which coalesced upon heating to 573 K, producing bimetallic particles surface-enriched in Rh. Homogenization of these particles did not occur until the temperature was raised above 773 K. De Jongste and Ponec (29), however, have noted that Pt-Au alloy particles on alumina are destroyed by oxidation but cannot be reformed by reduction (in contrast to the same alloy supported on SiO<sub>2</sub>). Therefore, as already stated by Sinfelt (24), oxidation is to be avoided if the

original clusters are to be preserved. Furthermore, calcination before reduction, frequently and effectively employed in catalyst preparation is probably undesirable if highly dispersed clusters are required: direct reduction of the precursor salts might be preferred.

#### ACKNOWLEDGMENTS

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