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# Effects of Oxidation and Reduction Treatments on Methylcyclopentane Hydrogenolysis over $Rh/TiO_2$ and $Rh/SiO_2$ Catalysts

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We have studied the effects of oxidation and reduction treatments of supported rhodium on its catalytic activity. In particular, we have studied the hydrogenolysis of methylcyclopentane over $Rh/SiO_2$ and $Rh/TiO_2$ catalysts with different metal dispersions. It has been observed that following oxidation at 673 K, a subsequent reduction at increasing temperatures causes a gradual increase in activity. When the reduction temperature reaches about 550 K a maximum in activity is observed, while a further increase in reduction temperature causes a decrease in activity. The same trend is observed on both $SiO_2$- and $TiO_2$-supported catalysts. However, the activity variations are most pronounced when the metal dispersion is high and the support is $TiO_2$. The changes in overall activity are accompanied by changes in selectivity. It is observed that the selectivity toward *n*-hexane follows the pattern opposite that of the activity, showing a minimum at reduction temperatures of about 550 K. Again, these selectivity variations are most pronounced for the titania-supported catalyst. We interpret these variations in terms of morphology changes occurring in the metal particles during the oxidation/reduction cycles. The reduction following the oxidation treatment initially renders the metal particles with a very open structure. Under these conditions the catalytic activity is relatively low. An increase in the reduction temperature causes an annealing of the metal particles, reaching an optimal configuration at about 550 K for which the catalytic activity shows a maximum. A further annealing of the metal particle caused by an increase in reduction temperature causes the activity to decrease. In the case of $TiO_2$, these changes are enhanced by an interaction occurring under high-temperature oxidation conditions between the oxidized Rh particles and the support. The behavior of the $TiO_2$-supported catalysts is also different at high reduction temperatures due to the well known SMSI effect.

## INTRODUCTION

In recent studies of supported rhodium catalysts (*1–4*) it has been demonstrated that high-temperature oxidation/reduction cycles cause profound changes in the morphology of metal particles. For example, it has been observed (*1*) that when a Rh particle supported on $SiO_2$ is oxidized and re-reduced, the original metal particle becomes broken into smaller particles, which subsequently may coalesce as the reduction temperature is increased. Lee and Schmidt (*1*) have noted that those morphology changes caused by thermal treatments may have strong effects on structure-sensitive reactions, such as hydrogenolysis of alkanes. In this contribution we analyze the effects that those morphology changes may have on the activity and selectivity of supported Rh catalysts for the hydrogenolysis of methyl cyclopentane (MCP). This reaction has been widely studied and is generally considered to be highly sensitive to the catalyst structure. Its product distribution has been found to markedly depend on the size of the metal particles. For instance, on Pt catalysts, large metal particles tend to mainly yield 2-methylpentane (2MP) and 3-methylpentane (3MP) as hydrogenolysis products, while small particles produce significant amounts of *n*-hexane (*5*). This reac-

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tion is also very sensitive to the presence of foreign species, such as carbonaceous deposits (*6*), a less active metal (*7*), or support species (*8*), on the metal surface. Therefore, it appears as an interesting test reaction for probing the proposed morphology changes.

If the support used is not inert under the conditions of the thermal treatments, its presence adds another complication to the analysis of the effects of such treatments. In the case of $TiO_2$ support, the effects of high-temperature reduction treatments have been extensively investigated in the recent past. It is now well established (*9*) that at sufficiently high reduction temperatures (typically 773 K, HTR) a partial encapsulation of the metal particles occurs. This phenomenon involves a surface migration of reduced species from the support and causes pronounced losses of catalytic activity and chemisorption capacity of the metals (*10, 11*). The catalyst is then considered to be in the so-called "SMSI state." It is also well known that an oxidation treatment at high temperatures (typically 673 K) reverses this state, in the sense that the original activity and chemisorption capacities are regained. Accordingly, in order to bring a catalyst from the "SMSI state" back to the "normal state," it has become a common practice to oxidize it at 673 K and subsequently reduce it at 473 K (LTR). However, in view of the morphology changes caused by similar thermal cycles on Rh particles supported on an inert support, such as $SiO_2$, it seems unlikely that the original structure of metal particles can be restored.

We have investigated three different samples, an impregnated 3% $Rh/SiO_2$, and ion-exchanged 0.3% $Rh/TiO_2$ and an impregnated 5% $Rh/TiO_2$. The first two have high metal dispersions while the third one has a significantly lower dispersion. Thus, we should be able to analyze the influence of oxidation/reduction cycles on a structure-sensitive reaction using different supports and metal particle sizes.

## EXPERIMENTAL

The 3% $Rh/SiO_2$ and 5% $Rh/TiO_2$ catalysts, identified here as 3RhS and 5RhT, respectively, were prepared by standard impregnation procedures. In both cases, aqueous solutions of $RhCl_3 \cdot 3H_2O$ were used for the impregnation with a liquid/support ratio of about 2.5 $cm^3/g$. The anion exchanged 0.3% $Rh/TiO_2$ catalyst, identified as 03RhT, was prepared as follows: the $TiO_2$ powder was placed in contact with a well stirred $6 \times 10^{-4}$ *M* $RhCl_3$ solution (pH 3.14) for 72 h using a solid/liquid ratio of 1 g $TiO_2$/60 $cm^3$. The mixture was subsequently centrifuged, filtered, and washed several times with distilled water until the supernatant liquid was colorless. The solid phase was then separated and left in air at room temperature until dry. The metal contents were determined by atomic absorption. The hydrogen chemisorption capacities of the catalysts were determined by the pulse technique, using pure $N_2$ as a carrier.

The catalysts were further characterized by temperature-programmed reduction (TPR) and catalytic activity measurements. The TPR apparatus used has been described elsewhere (*12*). A 5% $H_2/Ar$ stream was used as a reducing carrier at a total flow rate of 20 $cm^3$/min. The heating rate was 10 K/min. Before each TPR the catalyst sample was reduced at 773 K and oxidized in air at either 473 or 673 K. The effects of different oxidation/reduction cycles on sample 3RhS were analyzed by transmission electron microscopy (TEM) in a JEOL TEM 100CX. After each thermal treatment the samples were passivated in $H_2$ at 273 K, exposed to air at room temperature, crushed in a mortar, slurried in hydrogen peroxide, and deposited on a carbon film over a Cu grid.

The hydrogenolysis of methylcyclopentane was used as a test reaction. The activity measurements were performed in a microcatalytic pulse reactor. The oxidized samples were reduced *in situ* at various temperatures. In each run, a gaseous 250-$\mu$l

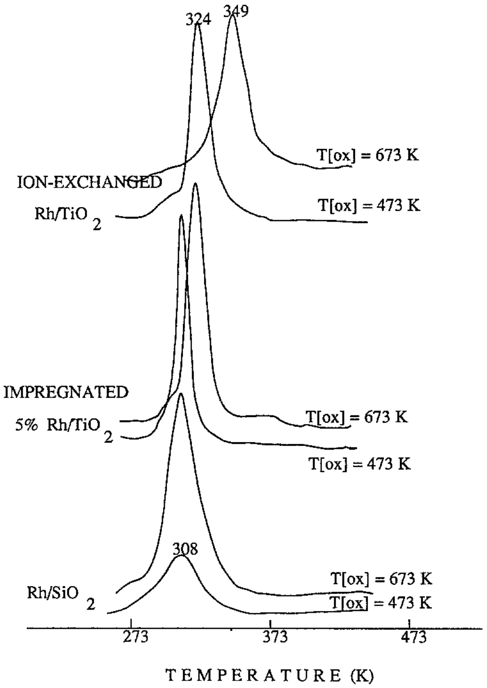

FIG. 1. Temperature-programmed reduction profiles. Hydrogen consumption as a function of temperature for catalysts 03RhT, 5RhT, and 3RhS after previous oxidation treatments at 473 and 673 K.

pulse of 6.8% MCP in hydrogen was injected into the $H_2$ stream which acted as a carrier. The products were analyzed by gas chromatography, using a DC200 column from Supelco.

## RESULTS

### *Temperature-Programmed Reduction*

Figure 1 shows TPR profiles obtained on samples 03RhT, 5RhT, and 3RhS after oxidation treatments at 473 and 673 K. A support effect is clearly evident. It is seen that an increase in the oxidation temperature has almost no effect on the position of the TPR peak for the 3RhS catalyst, while it causes significant changes in the TPR profiles of 5RhT and particularly 03RhT. For sample 3RhS a single reduction peak was observed at 308 K after both 473 and 673 K oxidation treatments. The reduction patterns of the $TiO_2$-supported catalysts are rather different. After oxidation at 473 K, sample 5RhT exhibits a single reduction peak at 310 K, about the same temperature as the one corresponding to sample 3RhS. But, after the 673 K oxidation, the main reduction peak appears shifted to a higher temperature, while only a small shoulder remains at 300–310 K. The 03RhT catalyst exhibits, after the 473 K oxidation, a main peak at 324 K with a shoulder at 300–310 K. The 673 K oxidation on this ion-exchanged catalyst causes a shift to higher reduction temperatures similar to that observed for the impregnated catalyst. However, in this case, the shift is more pronounced and the resulting peak is broader. At the same time, the size of the low-temperature shoulder is significantly reduced in comparison with the corresponding one following oxidation at 473 K.

Table 1 summarizes relative hydrogen consumptions measured by TPR for all the catalysts investigated. Rhodium contents in the catalysts, as measured by atomic absorption, and H/Rh ratios, as measured by hydrogen chemisorption after an oxidation/reduction cycle, are also included in Table 1. It is well known that the hydrogen consumption in the TPR experiments is related to the process of reduction of the rhodium, present as rhodium oxide ($Rh_2O_3$), to Rh metal. An increase in hydrogen consumption is evidenced for the impregnated catalysts 5RhT and 3RhS after the high-temperature oxidation compared with that measured after oxidation at 473 K. By contrast, no change was observed for the 03RhT catalyst. From the absolute values of hydrogen consumption during the TPR experiments after oxidation at 673 K, it can be concluded that in the three cases, all the Rh present in catalysts is first completely oxidized to $Rh_2O_3$ and subsequently completely reduced. In all the cases, the reduction is complete below 400 K. Therefore, the changes in hydrogen consumption observed for a given catalyst when varying the oxidation temperature can only be ascribed to differences in the degree of oxida-

TABLE 1

Rh Content (wt%) Measured by Atomic Absorption, Relative $H_2$ Consumption Measured by TPR, and H/Rh Measured by Pulse Chemisorption

| Catalyst | Rh content (wt%) | $H_2$ consump. (ox 473 K) / $H_2$ consump. (ox 673 K) | $H_2$ uptake[a] H/Rh |
|---|---|---|---|
| Rh/$SiO_2$ | 3.00 | 0.4 | 0.8 |
| Ion-exchanged Rh/$TiO_2$ | 0.3 | 1.0 | 2 |
| Impregnated Rh/$TiO_2$ | 4.95 | 0.8 | 0.4 |

[a] After oxidation at 673 K and reduction at 423 K.

tion of the particles, which in turn can be related to differences in the sizes of the rhodium particles present in both catalysts. A similar argument has been presented in Ref. (*13*). The larger particles are more difficult to oxidize; then the increase in hydrogen consumption with the preoxidation temperature observed for the impregnated catalyst can be due to the presence of large particles. Accordingly, the unchanged $H_2$ consumption observed for sample 03RhT is consistent with the small metal particles resulting from an ion exchange preparation.

### *Catalytic Activity*

We have investigated the catalytic properties of the three supported Rh catalysts by using the hydrogenolysis of methylcyclopentane as a test reaction. The only products detected were 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane, and small quantities of $C_1$–$C_5$ alkanes. Table 2 summarizes turnover numbers (TON) and product distribution for the catalysts investigated as measured in a pulse reactor after reduction at 473 K (LTR) and 773 K (HTR). We express all our TON based on the hydrogen chemisorption values obtained after LTR. As the product distribution varies with reaction temperature we report here data obtained at the same temperature (433 K) for every catalyst. The pulse reactor mode was used to minimize the effects of carbon deposition. No significant deactivation or changes in selectivity were detected between consecutive pulses. Similarly, no significant changes were found when the pulse size was varied.

The loss of activity commonly observed in SMSI catalysts after HTR is evident here for the $TiO_2$-supported catalysts. As previously noted (*10*), this effect is more pronounced for the better dispersed catalyst,

TABLE 2

Reaction Rates and Product Distribution for the Hydrogenolysis of Methylcyclopentane over Rh/$TiO_2$ and Rh/$SiO_2$

| Catalyst | Reduction temperature (K) | TON (at 433 K) × $10^3$ $sec^{-1}$ | Product distribution | | | |
|---|---|---|---|---|---|---|
| | | | 2MP | 3MP | Hx | $C_i$-$C_5$ |
| 3RhS | 473 | 30 | 81.1 | 11.2 | 5.0 | 2.7 |
| 03RhT | 473 | 20 | 86.0 | 12.0 | 2.0 | 0.0 |
| | 773 | 0.3 | 69.2 | 23.6 | 7.2 | 0.0 |
| 5RhT | 473 | 46 | 75.4 | 14.7 | 8.5 | 1.4 |
| | 773 | 3.5 | 75.0 | 18.0 | 7.0 | 0.0 |

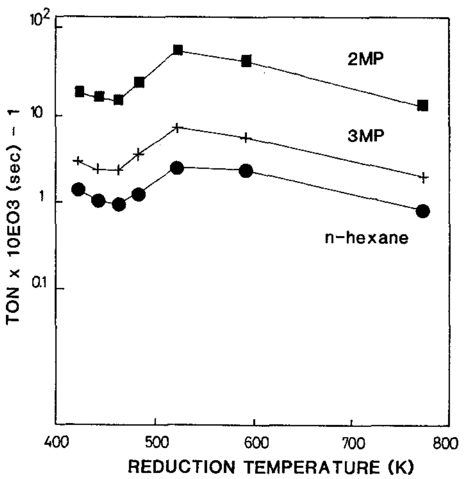

FIG. 2. Turnover numbers at 423 K for the hydrogenolysis of MCP as a function of reduction temperature after oxidation at 673 K over catalyst 3RhS.

in this case sample 03RhT. It is clear that even though the HTR may cause an increase in selectivity toward some products, it actually causes a decrease in the yield of all products. For instance, while the selectivity toward *n*-hexane over the 03RhT catalyst increases from 2 to 7%, the rate of *n*-hexane formation decreases from 4 × $10^{-4}$ to 2 × $10^{-5}$ $sec^{-1}$.

We have examined the variation of catalytic activity and selectivity as a function of reduction temperature after an oxidation treatment of the catalysts at 673 K for 1 h. Subsequently, the activity measurements were obtained at 423 K after reducing the sample for 30 min at the desired temperature. The results of these experiments for catalyst 3RhS are shown in Fig. 2. A strong dependence of the activity with the reduction temperature is observed. As the reduction temperature increases, the rate of formation of the three products initially increases, reaches a maximum at about 550 K, and then decreases. As shown in Fig. 3, a qualitatively similar pattern is exhibited by catalyst 03RhT. In this case, the activity also reaches a maximum at an intermediate reduction temperature. However, some important differences compared to the silica-supported catalysts may be noted. First, the 03RhT catalyst initially exhibits activity significantly lower than that of 3RhS, but it starts increasing at reduction temperatures significantly lower than those for 3RhS. In addition, the drop in activity observed for catalyst 03RhT following high-reduction temperatures is much more pronounced than that for the $SiO_2$-supported one. The results obtained for catalyst 5RhT are not shown, but its behavior was an intermediate between these two. The activity initially has a higher value, starts increasing at a higher temperature, and drops after the maximum in a less pronounced way than that of catalyst 03RhT. It then appears that the observed pattern depends on both the support and the metal particle size.

As shown in Fig. 4, the changes in activity are accompanied by changes in selectivity. As the reduction temperature increases the percentage of *n*-hexane in the products decreases, passes through a minimum, and then increases again. As for the total activity, the observed selectivity pattern is much more marked for the titania-supported catalysts, and particularly for the ion-exchanged one.

We have studied the morphological

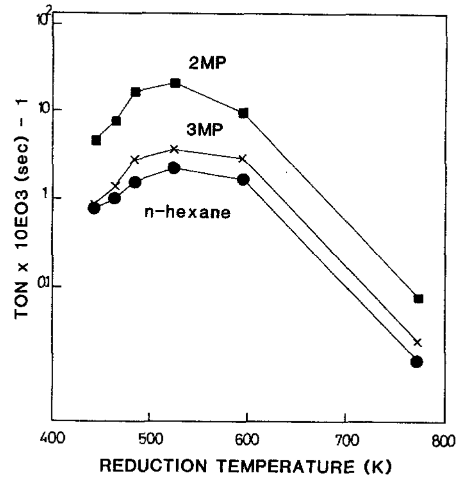

FIG. 3. Turnover numbers at 423 K for the hydrogenolysis of MCP as a function of reduction temperature after oxidation at 673 K over catalyst 03RhT.

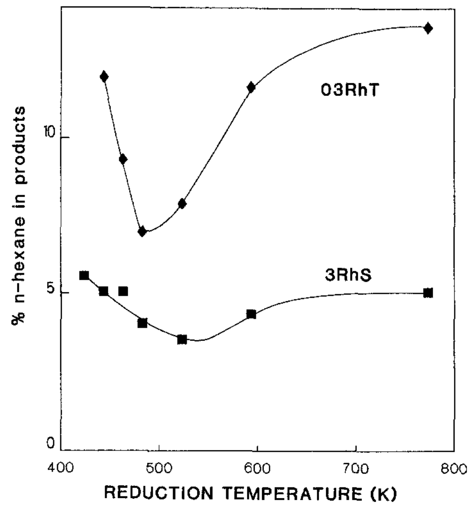

FIG. 4. Percentage of *n*-hexane in products at 423 K as a function of reduction temperature after oxidation at 673 K over catalysts 3RhS and 03RhT.

changes of the metal particles of catalyst 3RhS and the variation of its activity after several consecutive oxidation/reduction cycles. Micrograph A in Fig. 5 shows a view of the catalyst after oxidation at 673 K followed by reduction at 423 K. Micrograph B shows the same catalyst after five consecutive cycles of oxidation at 673 K/reduction at 773 K. Important differences are noted in the morphology of the rhodium particles on the two samples. It is clear that the metal particles in B exhibit significantly larger size, more regular shape, and higher contrast than those in A. Figure 6 shows the evolution of total activity of the 3RhS catalyst as a function of reduction temperature after oxidation at 673 K for several consecutive cycles. It is clear that the effect of reduction temperature over the activity becomes less pronounced after each cycle. In addition, the changes in selectivity also become less pronounced after each consecutive cycle.

## DISCUSSION

Let us first consider the behavior exhibited by the catalysts during the TPR experiment. As described above, the single reduction peak exhibited by the two impregnated catalysts after oxidation at 473 K can be ascribed to the reduction of relatively large $Rh_2O_3$ particles having a metallic core as a consequence of an incomplete oxidation. This metallic fraction may favor the reduction process. By contrast, on the ion-exchanged catalyst the oxidation of the rhodium particles at 473 K is complete. Thus, the shift to higher temperatures exhibited by this catalyst compared to the impregnated catalysts may just be due to the absence of a metallic core. However, the pronounced shifts observed for the $TiO_2$-supported catalysts after oxidation at 673 K should be associated with an interaction between the small aggregates of $Rh_2O_3$ and the surface of the $TiO_2$ support, which hinders the reduction process. Yao *et al.* (*14*) have shown that when $Rh/\gamma\text{-}Al_2O_3$ catalysts are treated in oxygen at high temperatures, a fraction of the rhodium interacts with the support and becomes more difficult to reduce. It has also been shown that Rh may even become buried in the support. This strong interaction has also been considered as the formation of a compound between the rhodium and the support (*15*). Such compounds have also been proposed to be formed under high-temperature oxidation conditions in other well dispersed systems, such as $Rh/Nb_2O_5$ (*16*) and $Ag/TiO_2$ (*17*) catalysts. Accordingly, the small peak at about 370 K observed for the impregnated catalyst as well as the main broad peak observed at 349 K for the ion-exchanged catalyst after the high temperature oxidation (673 K) would evidence a strong oxide–oxide interaction. Of course, this interaction would be more pronounced for the ion-exchanged catalyst, for which most of the rhodium is in close contact with the support. The small low-temperature shoulder exhibited by the ion-exchanged catalyst in the TPR following 473 K oxidation is an indication of the presence of three-dimensional clusters, which almost disappear after the oxidation at 673 K.

This interpretation appears at variance

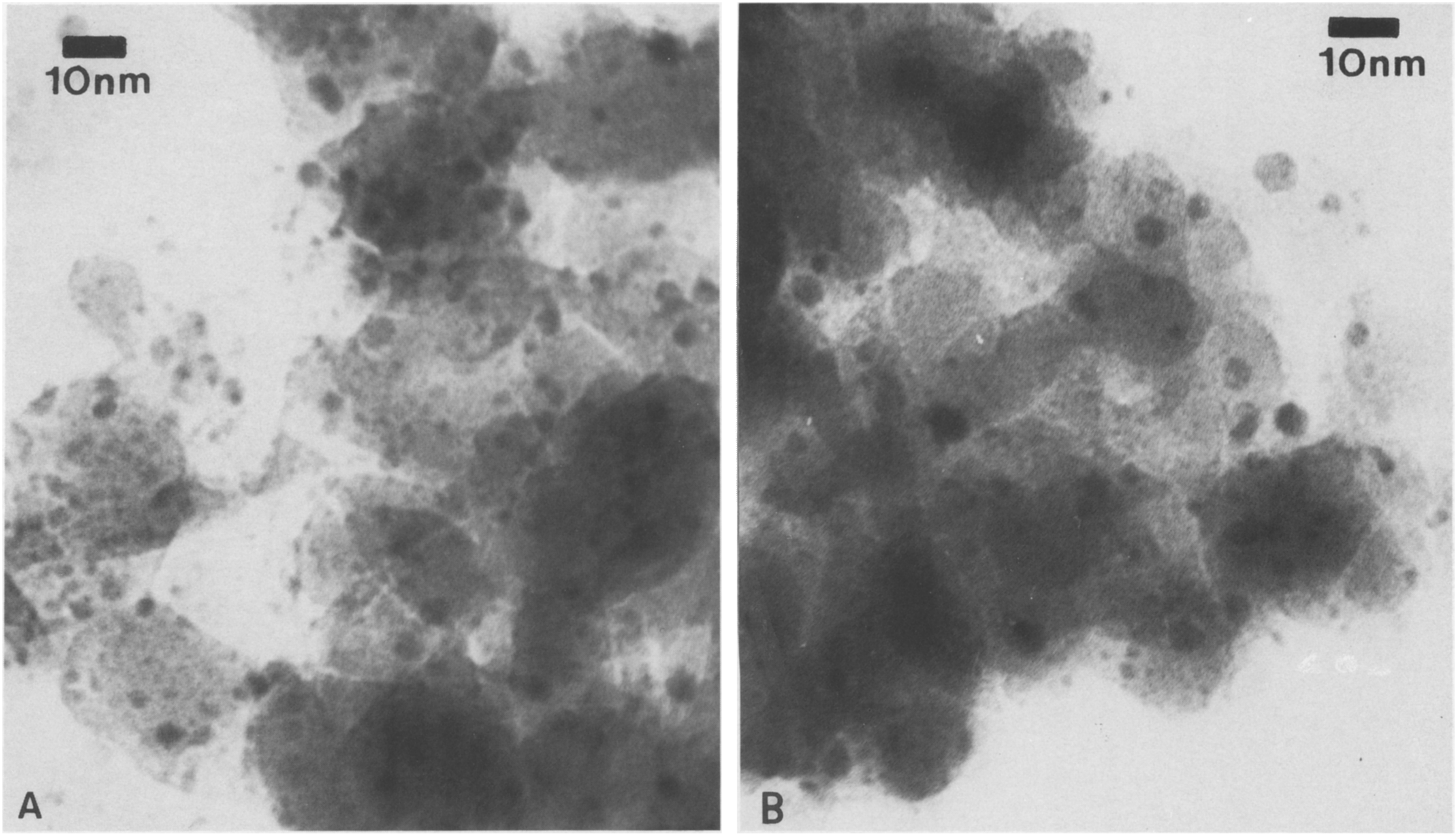

FIG. 5. Transmission electron micrographs of catalyst 3RhS. (A) Sample oxidized at 673 K and re-reduced at 423 K. (B) Sample oxidized and re-reduced at increasing temperatures (423 to 773 K) five times.

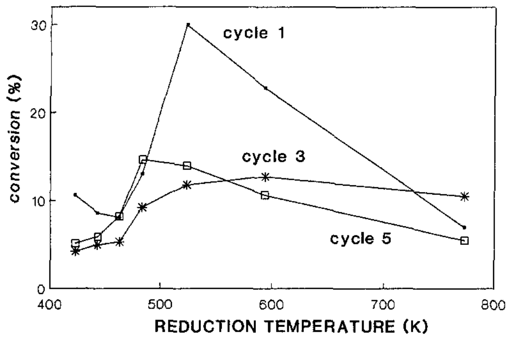

FIG. 6. Evolution of total activity of 3RhS catalyst at 423 K as a function of reduction temperature for several consecutive oxidation/reduction cycles.

with Vis *et al.* (*18*), who have also observed two reduction peaks in the TPR profiles of Rh/$TiO_2$ catalysts, one at 325 K and the other at 385 K, but have assigned the high-temperature one to the reduction of bulk-like $Rh_2O_3$ and the low-temperature one to better-dispersed $Rh_2O_3$. However, as has been recently demonstrated (*2*) the formation of well ordered crystalline $Rh_2O_3$, which is indeed more difficult to reduce, only occurs at oxidation temperatures above 875 K. On the other hand, our interpretation agrees well with results obtained by Pande and Bell (*19*). They have prepared a well dispersed 0.5% Rh/$TiO_2$ catalyst which exhibits a TPR peak shifted 20 K to temperatures higher than that corresponding to a 4.6% Rh/$SiO_2$ catalyst. This shift is of the same magnitude as the one we report here for the ion-exchanged catalyst oxidized at 473 K relative to the $SiO_2$-supported catalyst, while the oxidation at 673 K causes a further shift of about 25 K.

As illustrated in Figs. 2 and 3, we have observed that, after a high-temperature oxidation, the activity of all the rhodium catalysts investigated increases with reduction temperature until it reaches a maximum and then starts decreasing. As demonstrated by TPR the hydrogen consumption stops at temperatures significantly lower than 450 K. Therefore, the observed activity change cannot be attributable to a reduction process. We would rather ascribe this change in activity to a reconstruction of the metal particles associated with the oxidation/reduction cycle. We should interpret our results taking into account both the morphology changes inherent to the Rh particles themselves and the influence that an interaction with the support may have on those changes. Therefore, we will describe first the behavior of the $SiO_2$-supported catalyst and then that of the $TiO_2$-supported ones.

In a recent paper, Wong and McCabe (*2*) have examined the effects of oxidation/reduction treatments on the morphology of silica-supported Rh catalysts. They have observed that high-temperature oxidation treatments cause the formation of two types of Rh oxide particles. Some particles appear as well ordered crystalline $Rh_2O_3$ while others are composed by small $Rh_2O_3$ crystal domains aggregated in larger particles. The fraction of $Rh_2O_3$ present in the well ordered form is dominant at oxidation temperature above 1000 K. In the temperature range of our interest, i.e., below 673 K, most of the Rh oxide would be in the second form. They have also shown that a subsequent reduction at low temperature caused the formation of aggregates of small metal crystallites. We should take into account that during the oxidation treatment the metal particles undergo a significant volume expansion, which is expected to be reversed in the subsequent re-reduction. But, due to the low mobility of metallic Rh under LTR conditions, the metal particle is not completely annealed, and so an open structure with a roughened surface may result. This roughening process has been pointed out by Branschweig *et al.* (*3, 4*) to account for their HREM observations. It is therefore conceivable that, as the reduction temperature increases, this roughened surface starts becoming annealed; i.e., the density of more closely packed planes starts increasing. In agreement with this interpretation, recent XANES analyses

(*9e, 20*) have shown that an ion-exchanged $Rh/TiO_2$ catalyst exhibits a significant increase in the number of neighbors around the Rh absorber from LTR (473 K) to MTR (623 K), but little change between MTR and HTR (773 K). Our own TEM micrographs support this idea. When the 3RhS sample was oxidized at 673 K and reduced at 423 K (micrograph A) it exhibited a high density of small metal aggregates. These aggregates have a much lower contrast and more irregular shape than those in micrograph B, which represents the same catalyst after several thermal cycles. The higher contrast and regularity of the particles in B would be a consequence of the proposed process of annealing taking place during the thermal cycle.

Therefore, based on this picture we propose that the activity increase observed when the reduction temperature goes from 423 to 533 K is due to a surface annealing process. It is generally accepted that hydrogenolysis reactions require a large ensemble of metal atoms to constitute the active site. Accordingly, as a roughened surface is progressively "healed," an increase in activity is expected. A similar hypothesis has been recently proposed by Nuñez *et al.* (*13*) to explain increases in hydrogenolysis activity of $Rh/Al_2O_3$ catalysts as the reduction temperature increases.

The occurrence of activity maxima as a function of reduction temperature for all the catalysts investigated would suggest that through the process of annealing described above the metal surface passes through an optimal configuration for catalytic activity. Beyond that point further annealing of the surface makes the activity decrease. This hypothesis is sustained by the fact that after successive thermal cycles the activity not only decreases but its variations with reduction temperature are less marked (see Fig. 6). As shown in Fig. 5 after several cycles a particle growth and an ordering of the metal particles are evident. Thus, the effects of the proposed transformation are expected to be less pronounced.

Goodman (*21, 22*) has emphasized the importance of the spacing between surface atoms in determining the catalytic activity. He has measured the specific activity of the Ni (100) and (111) planes for ethane, *n*-butane, and cyclopropane hydrogenolysis. It is observed that the open fcc (100) surface exhibits a much higher activity for C–C bond breaking than that of the close-packed (111) surface. He points out that the C–C bond length of the reaction intermediate is about the same as the spacing between high-coordination sites on the Ni (111) surface, but it is significantly shorter than the spacing between four fold sites on the (100) surface. It is then reasonable to expect that on the former the C–C bond would tent to remain intact while on the latter it should break more easily. A conversion at high reduction temperatures of open planes, such as the fcc (100), into more closely packed ones, as the fcc (111), is thermodynamically favored and has been experimentally confirmed. For instance, Yacamán and Gómez (*23*) have observed a conversion of (100) facets into (111) planes in a Ni/graphite catalyst as the reduction increases.

Based on these ideas we can propose three different states of the metal particles as the reduction temperature is increased after high-temperature oxidation. At low reduction temperatures, e.g., 423 K, the metal surface would exhibit a very open structure with low activity for MCP hydrogenolysis because the density of active sites comprising a large ensemble of atoms is low. As the reduction temperature increases to about 550 K an optimal surface arrangement for catalytic activity is obtained. Finally, at higher reduction temperatures the surface becomes more closely packed and, consequently, less active.

Since smaller patterns are obtained on either $SiO_2$- or $TiO_2$-supported catalysts it would seem that the sequence of morphology changes described above do not necessarily depend on the type of support used. However, our TPR profiles show profound changes caused by the high-temperature oxidation (673 K) on the reduction ability of the $TiO_2$-supported catalysts which are not observed for the $SiO_2$-supported ones. These changes are most pronounced for the ion-exchanged catalyst, which would indicate that the interaction with the support is more evident when the metal particles are small. This interaction may be responsible for the differences observed by comparing Figs. 2 and 3. As shown by Schmidt *et al.* (*24, 25*), during oxidation treatments Rh particles supported on oxide substrates tend to expand parallel to the surface, while a subsequent reduction causes the disruption of the metal particles into small crystallites. These authors ascribed this process to a stronger interaction between the metal oxide and the substrate than between the metal and the substrate. In the case of $SiO_2$ support this effect was only evident at oxidation temperatures of about 870 K. As suggested by our TPR experiments, the interaction of the $Rh_2O_3$ particles with $TiO_2$ may start at significant lower oxidation temperatures. This interaction may make the rhodium particles spread more effectively over the $TiO_2$ surface than over that of $SiO_2$. Then, the $TiO_2$-supported Rh particles after low-temperature reduction are expected to have a more open structure than those of $SiO_2$. This would explain the lower initial activity of the 03RhT catalyst and its more rapid response to the increase in reduction temperature compared to that of 3RhS.

As the reduction temperature is increased above 550 K the so-called SMSI effect should also be considered for the $TiO_2$-supported catalysts. It is well known (*10*) that in the presence of hydrogen at increasing temperatures, titanium suboxide species progressively cover the metal particle surface, causing the observed decrease in catalytic activity. This effect on $Rh/TiO_2$ catalysts has been demonstrated to start affecting hydrogenolysis activity at reduction temperatures as low as 540 K (*26*) and is most pronounced for the small particles. Therefore, on these catalysts it may be the main cause of the sharp activity drop which occurs at high reduction temperatures.

Finally, it is interesting to analyze the variation of selectivity through the oxidation/reduction cycles. The hydrogenolysis of MCP is believed to proceed through two different reaction paths. The first one, which is called the selective mechanism, mainly yields 2MP and 3MP (*27*). This mechanism would involve a tetra-adsorbed intermediate which could be preferentially formed on highly coordinated surface atoms. In the case of Pt, this hypothesis is consistent with the experimental fact that on large metal particles and on low-index crystal faces, the main products of the MCP hydrogenolysis reaction are 2MP and 3MP. On the other hand, the nonselective mechanism, which would give the three products in the statistical distribution, 2MP : 3MP : Hx (40 : 20 : 40), would take place on low-coordinated surface atoms. In this case, the intermediate $C_5$ ring would be bound to a single atom. For rhodium catalysts the situation appears to be somewhat less clear. The few works reporting particle size effects on the selectivity of this reaction over Rh are not conclusive. Del Angel *et al.* (*28*) have observed an increase in selectivity toward *n*-hexane with decreasing Rh particle size in Rh/alumina catalysts. By contrast, Anderson *et al.* (*29*) have suggested that the larger particles in Rh/titania catalysts produce more *n*-hexane. In these cases, however, the effects of carbon deposition pointed out by van Senden *et al.* (*6*) should be considered. These authors have indicated that a blocking layer of carbon residues can lead to a suppression of the overall activity with a relative enhancement of the selectivity toward *n*-hexane formation. As the carbon deposition depends on particle size it may mask the real particle size effect on selectivity. In our case, we have minimized the carbon deposition problem by using the pulse method for the catalytic activity determinations. By continuously flowing pure

$H_2$ at the reaction temperature, this method allows the catalyst surface to remain free of hydrocarbon residues.

If, as we propose above, the initial increase in reduction temperature following oxidation causes the annealing of a roughened Rh surface, we can expect that an increase in the number of large metal ensembles may occur. Accordingly, the more marked change observed for 2MP (see Figs. 2 and 3) would suggest that the ensemble required to produce this molecule would be larger than that required to produce the others. As pointed out by Ponec (*5, 6*), the three products can be formed through single-site complex intermediates, but only 2MP and 3MP can be formed through multisite intermediates. The multisite complexes are more easily formed. Then, when a sufficiently large ensemble of atoms is available the production of 2MP and 3MP dominates. Accordingly, as shown in Fig. 3 the effect of $TiO_2$ is shown once again by the sharper decrease in selectivity toward *n*-hexane as the reduction temperature increases. It is interesting to note that not only the Hx/2MP ratio but also the 3MP/2MP ratio varies with the reduction temperature and the catalyst being studied. The 3MP/2MP ratio is always smaller than the statistical value of $\frac{1}{2}$ and it increases for catalysts in the SMSI state. On the basis of the observed Hx/2MP ratio, at the lowest reduction temperatures, we can conclude that the Rh particles in catalyst 03RhT must be more open, less active, and more selective to Hx than those in catalyst 5RhT or 3RhS. When the reduction temperature is high enough to cause the migration of $TiO_x$ species onto the metal particles (SMSI effect), the increase in the Hx/2M ratio can be ascribed to a disruption of the larger ensembles, required for 2MP formation, by the presence of the support species. Resasco and Haller (*10*) have emphasized the similarities exhibited by catalysts in the SMSI state and group VIII–group Ib metal catalysts. This analogy is evidenced once more here as we compare the increase in the Hx/2MP ratio observed for our catalyst as the reduction temperature increases with that of Pt catalysts alloyed with Au (*7*).

## CONCLUSIONS

The main conclusions of this work can be summarized as follows:

(a) after oxidation of $Rh/SiO_2$ and $Rh/TiO_2$ catalysts at 673 K, the subsequent reduction at increasing temperatures initially causes an increase in the activity for the methylcyclopentane hydrogenolysis. A maximum is reached at about 550 K. A further increase in reduction temperature causes a decrease in activity.

(b) the changes in activity are accompanied by changes in selectivity. The percentage of *n*-hexane in products decreases as the reduction temperature increases, reaches a minimum, and then increases again at high reduction temperatures.

(c) similar patterns are obtained on both $Rh/SiO_2$ and $Rh/TiO_2$ catalysts, but they are more pronounced on the $TiO_2$-supported ones.

(d) the changes in catalytic properties are interpreted in terms of changes in morphology of the metal particles observed by TEM after the successive thermal treatments. Following the high-temperature oxidation the subsequent reduction leaves the metal particles with a very open structure. The catalytic activity of this surface would be relatively low. An increase in the reduction temperature causes an annealing of the metal particles, reaching an optimal configuration which would show the maximum catalytic activity. A further annealing of the metal particle caused by an increase in reduction temperature causes the activity to decrease.

(e) these changes are more marked on $TiO_2$-supported catalysts due to an interaction occurring under high-temperature oxidation conditions between the oxidized Rh particles and the support shown by TPR experiments.

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