JOURNAL OF CATALYSIS **127**, 276–286 (1991)

A Comparison of Niobia- and Vanadia-Promoted Rh Catalysts: The Behaviors of RhMO$_4$ (M = Nb, V) on SiO$_2$ during Calcination and Reduction Treatments

Z. HU, T. WAKASUGI, A. MAEDA, K. KUNIMORI,* AND T. UCHIJIMA

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received May 9, 1990; revised August 17, 1990

The behaviors of Nb_2O_5 and V_2O_5 in Rh/SiO$_2$ catalysts are compared by X-ray diffraction. For vanadia-promoted Rh/SiO$_2$ catalyst, $RhVO_4$ compound was formed exclusively by mild calcination at 773 K, and larger crystallites formed by calcination at 973 K. For niobia-promoted Rh/SiO$_2$ catalysts, $RhNbO_4$ compound was formed almost exclusively after the high-temperature calcination at 1173 K. The $RhVO_4/SiO_2$ and $RhNbO_4/SiO_2$ catalysts exhibit significant SMSI behaviors after high-temperature reduction, typically at 773 K; the capacity of H_2 chemisorption diminished almost to zero and the catalytic activity for ethane hydrogenolysis was suppressed by ca. 3.5 orders of magnitude as compared with that after the low-temperature reduction that followed. Redispersion of rhodium was observed during the decomposition of compounds in H_2. Large $RhNbO_4$ particles (139 Å) split to a number of smaller Rh particles (48 Å) after the H_2 reduction at 773 K, and niobia promoter stabilized such Rh particles which exhibited almost no agglomeration during the thermal treatment in He even at 973 K. Similar redispersion was observed for $RhVO_4$ compound, and large particles (190 Å) split to smaller Rh particles with mean size of 40 Å after the H_2 reduction at 773 K. However, such Rh particles agglomerated to large ones (122 Å) by the thermal treatment at 973 K. V_2O_5 reacted with Rh at much lower temperature than Nb_2O_5, with large Rh particles being converted to $RhVO_4$ compound even by the mild calcination at 773 K. This phenomenon may find practical application in the regeneration of sintered Rh catalyst.

INTRODUCTION

There has been much interest in the effects of additives of transition metal oxides on the catalytic properties of group 8 metals especially in CO hydrogenation reaction (*1–7*). Higher catalytic activity was observed for metal catalysts supported on such oxides in comparison with silica and alumina supports (*8*). The metal catalysts supported on transition metal oxides usually exhibit a significant suppression in the ability of H_2 chemisorption and the catalytic activity for ethane hydrogenolysis after high-temperature reduction (HTR) at 773 K (SMSI behaviors) (*9–12*). At the present time, it is generally accepted that a partially reduced oxide species is formed during the HTR treatment, and then covers the surface of the metal particle to cause the decrease of chemisorption ability and activity (decoration model) (*13–23*). For the promoted metal catalysts, in which transition metal oxide was used as a promoter, significant SMSI behavior has been observed in TiO_2-, V_2O_5-, and Nb_2O_5-promoted Rh/SiO$_2$ catalysts (*24–27*). At the same time, these oxides are also known to promote the catalytic activity of Rh metal in CO hydrogenation (*28–31*). These additive effects should be due to the interaction between metal and oxide promoter, although the mechanism could be different among them.

In the previous papers, we have found a formation of $RhNbO_4$ compound in the niobia-promoted Rh/SiO$_2$ catalyst (*27*), and the $RhNbO_4/SiO_2$ catalyst exhibited the significant SMSI behaviors after the decompo-

---

*To whom correspondence should be addressed.

0021-9517/91 $3.00

sition of the compound by H_2 reduction at 773 K (*32, 33*). Formation of $RhVO_4$ compound has been postulated in the vanadia-promoted Rh catalysts (*34*), which exhibited a promoted activity in CO hydrogenation relative to unpromoted Rh catalysts (*31*). Vanadium and niobium are similar in electronic structure, and both oxides (V_2O_5 and Nb_2O_5) can form $RhMO_4$ (M = V or Nb) compounds with rhodium. It would thus be interesting to compare the effects of the two oxides as promoters. This work has been undertaken to study the formation and decomposition of the Rh double oxide ($RhMO_4$) on SiO_2 to obtain more insight concerning the metal-oxide interaction on supported metal catalysts (*32, 33*).

In this paper, the focus is on the comparison of the behaviors of vanadia and niobia promoters in Rh/SiO_2 catalyst during calcination, reduction, and thermal treatment.

EXPERIMENTAL

Preparation of catalysts. Two SiO_2 supports (denoted as SIO-3 and SIO-4) were provided as Japan Reference Catalyst (JRC) (*35*). The BET surface areas of SIO-3 and SIO-4 were 186 and 373 m^2/g, respectively. Before the loading of metal and promoter, the silica supports were precalcined in air at 1173 K for 3 h to avoid possible structural change during the following high-temperature calcination. The BET surface area decreased to 40 m^2/g for SIO-3, and to 270 m^2/g for SIO-4, respectively. Silica-supported 4.2 wt% Rh catalysts were prepared by impregnation of the precalcined supports with a solution of $RhCl_3$, then dried at 393 K but not calcined. These samples were then impregnated with $(NH_4)_3[NbO(C_2O_4)_3]$ or NH_4VO_3 dissolved in deionized water, and dried at 393 K overnight. The non-, niobia-, and vanadia-promoted Rh catalysts were obtained by calcining the samples in air at desired temperature (773 K for 1 h, and 973 and 1173 K for 3 h). For the promoted Rh catalysts, the Nb_2O_5 and V_2O_5 loading were chosen so that the atomic ratio of Nb/Rh and V/Rh is unity, respectively.

H_2 chemisorption. Volumetric H_2 chemisorption was measured in a conventional glass vacuum system, as described before (*27*). The catalyst was pretreated in O_2 at 773 K for 1 h, followed by low-temperature reduction at 373 or 473 K (LTR) or high-temperature reduction at 773 K in H_2 flow purified with a liquid nitrogen trap. Before the measurement of H_2 adsorption at room temperature, the catalyst was evacuated *in vacuo* at the catalyst reduction temperature for 1 h.

Ethane hydrogenolysis. The catalytic activity measurements for the ethane hydrogenolysis reaction were performed in a microcatalytic pulse reactor. The details of the procedure were described elsewhere (*27*). The reaction was carried out after the same pretreatments as in the chemisorption measurements.

X-ray diffraction. The XRD measurements were performed with an X-ray diffractometer (Rigaku Co. Ltd.) with a graphite monochromator for Cu$K\alpha$ (40 kV, 30 mA) radiation. An on-line computer was used for data collection and processing, which allowed precise determination of *d* spacing values from the diffraction lines. For normal measurements, a slower scan speed (0.5 degree/min) was used.

RESULTS

Catalytic Properties

The catalytic properties of Rh catalysts are presented in Table 1. The calcined catalyst was first reduced in H_2 at 773 K before any adsorption and activity measurements. This H_2 treatment was performed to decompose the $RhNbO_4$ and $RhVO_4$ compounds, which were formed by the high-temperature calcination, as presented later. It can thus be considered that the obtained chemisorption capacity and activity are the catalytic properties of the Rh metal particles.

For the unpromoted Rh/SIO-3 catalyst calcined at 1173 K, a small decrease of about 0.4 order of magnitude was observed in the catalytic activity for ethane hydrogenolysis after the HTR at 773 K relative to the follow-

TABLE 1

Catalytic Properties of Vanadia- and Niobia-Promoted Rh Catalysts

Catalyst	Calcination temperature (K)	H/Rh[a] (1) 773 K	H/Rh[a] (2) 373 K	H/Rh[a] (3) 473 K	$\log(r_{HTR}/r_{LTR})$[b]	Mean size of[c] Rh particles (Å)
Rh/SIO-3	1173	0.074	0.074	—	−0.4	134
Nb_2O_5–Rh/SIO-3	1173	0.004	0.140	0.110	−3.5	48
Nb_2O_5–Rh/SIO-4	1173	0.008	—	0.103	−3.4	40
V_2O_5–Rh/SIO-3	973	0.006	0.100	0.132	−3.5	43

[a] The calcined catalyst was first reduced in H_2 at 773 K before adsorption and activity measurements. The H_2 adsorption measurements were made according to the following sequence: (1) H_2 reduction at 773 K, (2) 373 K, (3) 473 K.

[b] Catalytic activity for ethane hydrogenolysis (r_{HTR}) was measured after the calcined catalyst was reduced in H_2 at 773 K. The catalyst was then treated in O_2 at 673 followed by low-temperature reduction (LTR) in H_2 at 373 K before the activity measurement of r_{LTR}.

[c] The mean size of Rh particles was obtained from X-ray diffraction pattern of the catalyst reduced in H_2 at 773 K according to the Scherrer formula.

ing LTR at 373 K. Similar effects have been reported for ethane hydrogenolysis reaction by Lee and Schmidt (*36*), who suggested that such variations in catalytic activity were caused by morphology changes of Rh particles. Drastic decreases were observed for the niobia- and vanadia-promoted Rh catalysts; that is, the suppression of 3.5 orders of magnitude for the niobia-promoted Rh/SIO-3 catalyst calcined at 1173 K, 3.4 for the niobia-promoted Rh/SIO-4 catalyst calcined at 1173 K, and 3.5 for the vanadia-promoted Rh/SIO-3 catalyst calcined at 973 K, as compared with those after the following O_2 treatment at 673 K and successive LTR at 373 K. Such severe suppression of activity after HTR should be related to the strong Rh–Nb_2O_5 or Rh–V_2O_5 interaction, because no drastic change was observed for the unpromoted Rh catalyst (*27*).

The results of H_2 chemisorption and XRD studies are also shown in Table 1. For the Rh/SIO-3 catalyst, rhodium sintered severely during the calcination at 1173 K. The mean size of Rh particles is 134 Å after the H_2 reduction at 773 K according to Scherrer formula of X-ray diffraction. However, much smaller Rh particle size was obtained for the promoted Rh catalysts, though they also experienced high-temperature calcination (973, 1173 K). For instance, the niobia-promoted Rh/SIO-3 catalyst exhibited the mean size of about 48 Å after the H_2 reduction at 773 K. The capacity of H_2 chemisorption diminished almost to zero after the HTR at 773 K, although the Rh dispersion was 0.2 according to X-ray diffraction, and it was recovered to 0.14 in H/Rh value by the O_2 treatment at 773 K followed by the LTR at 373 K. Quite similar results were also obtained in the niobia-promoted Rh/SiO-4 calcined at 1173 K and the vanadia-promoted Rh/SIO-3 catalyst calcined at 973 K.

Rh/SiO$_2$ Catalyst

The XRD patterns of Rh/SIO-3 catalyst after air calcination at different temperatures are presented in Fig. 1. The broad background peak at around 20° is due to the amorphous SiO_2. Only a few broad diffraction peaks probably corresponding to Rh_2O_3 phase were observed after being calcined in air at 773 K (no. 1). The diffraction lines of Rh_2O_3 became more clear and sharper by the calcination temperature increase (no. 2 at 973 K and no. 3 at 1173 K), due to the sintering of Rh_2O_3 particles. Only the Rh_2O_3 phase was observed even when the Rh/SIO-

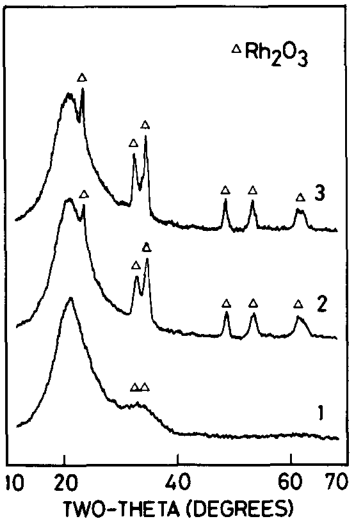

FIG. 1. X-ray diffraction patterns of Rh/SIO-3 catalyst after being calcined in air at different temperatures. (1) 773 K, (2) 973 K, (3) 1173 K.

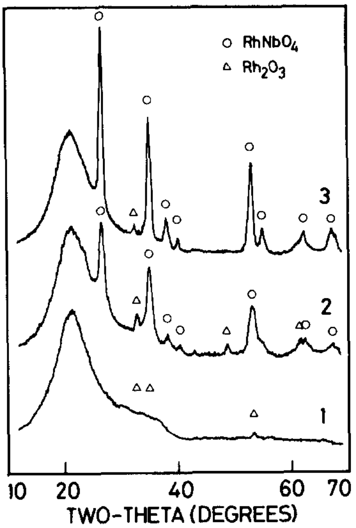

FIG. 2. X-ray diffraction patterns of Nb_2O_5–Rh/SIO-3 catalyst after being calcined in air at different temperatures. The atomic Nb/Rh ratio is unity. (1) 773 K, (2) 973 K, (3) 1173 K.

3 catalyst was calcined at 1173 K. This suggests that no chemical reaction occurs between rhodium and silica support.

Niobia-Promoted Rh Catalysts

The XRD patterns of the niobia-promoted Rh/SIO-3 catalyst after air calcination at different temperatures are presented in Fig. 2. After the calcination at 773 K, there are only a few broad diffraction peaks which can be assigned to Rh_2O_3 phase. Rh_2O_3 and $RhNbO_4$ phases are observed clearly after the calcination at 973 K. At 1173 K, the diffraction peaks of $RhNbO_4$ became sharper and increased substantially in their intensities. The results imply that more rhodium and niobia promoter migrated to each other to form $RhNbO_4$ compound during the calcination at higher temperature. Similar results were observed for the niobia-promoted Rh/SIO-4 catalyst.

Vanadia-Promoted Rh Catalyst

Figure 3 shows the XRD patterns for the vanadia-promoted Rh/SIO-3 catalyst after air calcination at different temperatures. After the calcination at 773 K, a number of sharp diffraction peaks appeared, but there are no diffraction peaks corresponding to Rh_2O_3 phase. The small diffraction peak at 15.35° ($d = 5.767$ Å) can be attributed to the (200) line of the V_2O_5 phase, while no other

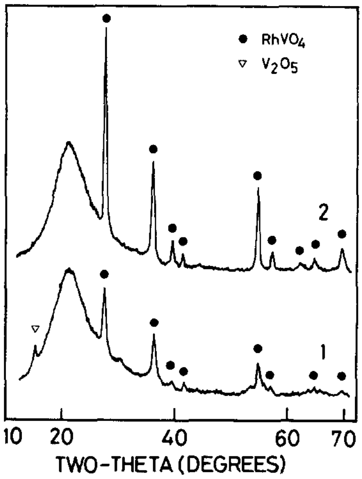

FIG. 3. X-ray diffraction patterns of V_2O_5–Rh/SIO-3 catalyst after being calcined in air at different temperatures. The atomic V/Rh ratio is unity. (1) 773 K, (2) 973 K.

TABLE 2

Observed and Calculated *d* Spacing Values (Å) for the New Phase in the Vanadia-Promoted Rh Catalyst after being Calcined in Air at 973 K

$d_{exp.}$	I/I_1	*h k l*	$d_{cal.}{}^{a}$
3.223	100	1 1 0	3.223
2.489	54	1 0 1	2.489
2.272	20	2 0 0	2.279
2.182	17	1 1 1	2.184
2.038	13	2 1 0	2.038
1.678	50	2 1 1	1.681
1.609	18	2 2 0	1.611
1.489	13	0 0 2	1.486
1.438	15	3 1 0	1.441
1.350	22	3 0 1	1.353
1.245	11	1 1 2	1.224

[a] The *d* spacing values were calculated by assuming that the new phase takes the tetragonal structure of $RhNbO_4$ compound. The *a* and *c* values were calculated to be 4.558 and 2.971 Å, respectively.

diffraction lines of this phase exist. All other diffraction peaks can be attributed to a new phase between rhodium and vanadia promoter, the intensity of which increased substantially by the calcination at 973 K. For these new diffraction peaks, a best fit was obtained by assuming the tetragonal $RhNbO_4$-type structure of the values of lattice constants of a = 4.558 and c = 2.971 Å as shown in Table 2. Therefore, it may be justified that the appearance of new diffraction peaks is ascribed to the formation of $RhVO_4$ compound. Shaplygin *et al.* (*37*) have reported the crystal structure of unsupported $RhVO_4$ compound, which is in good agreement with the present analysis.

Decomposition of $RhNbO_4$ Compound in Hydrogen

For the niobia-promoted Rh catalysts, $RhNbO_4$ compound was formed almost exclusively on silica surface by the calcination at 1173 K. The sharp diffraction peaks imply that $RhNbO_4$ compound agglomerated to large crystallites during the calcination. The structure change of this compound in H_2 was studied by X-ray diffraction, as shown in Fig. 4. For the niobia-promoted Rh/SIO-4 catalyst calcined at 1173 K, no structure change was observed by the H_2 reduction at 373 K (no. 1). The Rh_2O_3 phase (the small diffraction peak at 32.81 degree) as a minor constituent was reduced to Rh metal in H_2 at 473 K (no. 2). The decomposition of $RhNbO_4$ compound was initiated by the H_2 reduction at 573 K, where a mixture of $RhNbO_4$ compound and Rh metal is observed (no. 3). After the treatment in H_2 at 673 K, only the broad diffraction peaks corresponding to Rh metal are observed (no. 4). This result indicates that $RhNbO_4$ compound was reduced completely, and the large $RhNbO_4$ particles split to a number of smaller Rh particles during the reduction treatment at 673 K. A similar XRD profile with a small peak due to NbO_2 is also observed after the reduction at 773 K (no. 5). When the catalyst was treated in He at 973 K following the H_2 reduction at 773 K, the diffraction peaks of NbO_2 phase became

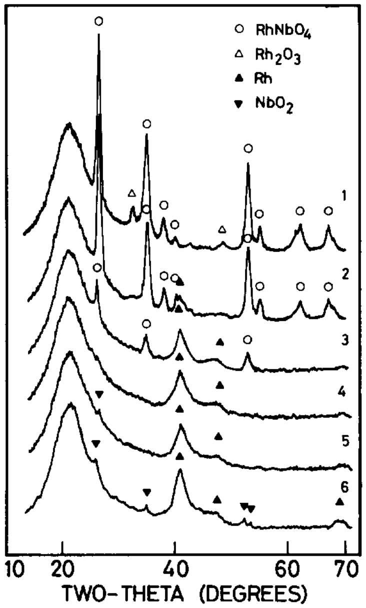

FIG. 4. Decomposition of $RhNbO_4$ compound in H_2. The $RhNbO_4$/SIO-4 catalyst was treated in H_2 at: (1) 373 K, (2) 473 K, (3) 573 K, (4) 673 K, (5) 773 K, (6) in H_2 at 773 K and in He at 973 K.

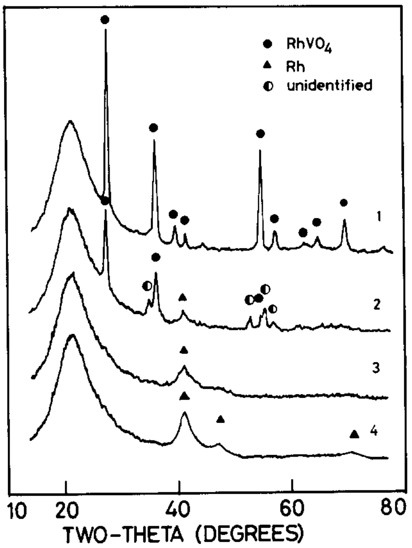

FIG. 5. Decomposition of $RhVO_4$ compound in H_2. The $RhVO_4$/SIO-3 catalyst was treated in H_2 at: (1) 373 K, (2) 473 K, (3) 573 K, (4) 773 K.

clear, certainly due to the agglomeration of small NbO_2 particles. However, almost no change was observed in the diffraction pattern of Rh metal (no. 6).

Decomposition of $RhVO_4$ Compound

For the vanadia-promoted Rh catalyst, $RhVO_4$ compound was formed exclusively on silica surface after being calcined at 973 K (Fig. 3). The decomposition of this compound in hydrogen was studied by X-ray diffraction. As shown in Fig. 5, no reduction in the diffraction intensity of $RhVO_4$ compound was observed by the reduction at 373 K (no. 1). The decomposition was initiated at 473 K in H_2 (no. 2). Most of the $RhVO_4$ compound was reduced to Rh metal and an unidentified phase, which may correspond to partially reduced vanadium oxide. The decomposition and further reduction of the compound and the unidentified phase were completed by the H_2 reduction at 573 K, with only a broad diffraction peak of Rh metal being observed (no. 3). No vanadium oxide could be detected by X-ray diffraction, probably due to its redispersion to amorphous phase during the decomposition process.The H_2 reduction at 773 K gave a similar profile, though the diffraction peaks of Rh metal became sharper (no. 4). These behaviors are similar to those of the niobia-promoted Rh catalysts; that is, the large $RhVO_4$ particles split into a number of smaller Rh particles during the decomposition process, as implied by the sharp diffraction peaks of $RhVO_4$ compound before H_2 treatment and the broad peaks of Rh metal after decomposition of the compound.

The XRD pattern of the reduced $RhVO_4/SiO_2$ catalyst was also recorded after the following He treatment at 973 K. As shown in Fig. 6 (no. 2), the diffraction peaks of Rh metal became much sharper by this thermal treatment (no. 2). The mean size of Rh particles is 122 Å. In addition, there appeared three small diffraction peaks (d = 2.719, 2.480, and 1.702 Å), which can be attributed to the three most intensive diffraction lines of V_2O_3 phase (no. 2). For comparison, the diffraction pattern of Rh/SIO-3 catalyst calcined at 1173 K and then reduced in H_2 at 773 K is also shown in Fig. 6 (no. 1). The

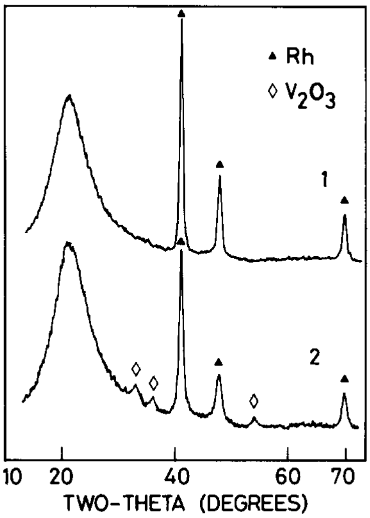

FIG. 6. X-ray diffraction patterns of Rh catalyst. (1) 4.1% Rh/SIO-3 catalyst, calcined in air at 1173 K, reduced in H_2 at 773 K. (2) $RhVO_4$/SIO-3 catalyst treated in H_2 at 773 K, and then in He at 973 K.

mean size of Rh particles is 134 Å (Table 1). Both the catalysts exhibited almost the same sharp XRD peaks of Rh metal, which indicate that Rh particles of both catalysts sintered severely by the high-temperature thermal treatment.

Redispersion of Rh Metal

After the $RhNbO_4$ and $RhVO_4$ compounds have been once decomposed to Rh metal by the H_2 reduction at 773 K, the structure changes of the catalyst during recalcination in O_2 were characterized by X-ray diffraction as shown in Fig. 7. The $RhNbO_4$/SIO-3 (calcined at 1173 K) and $RhVO_4$/SIO-3 (calcined at 973 K) were used as starting materials.

For the niobia-promoted Rh/SIO-3 catalyst, most of the Rh metal obtained by the H_2 reduction at 773 K were oxidized to Rh_2O_3 during the following O_2 treatment at 773 K (no. 1). A small diffraction peak of $RhNbO_4$ compound and a few broad peaks of Rh metal were also observed in this profile. In the XRD pattern no. 2, the catalyst was pretreated in He at 973 K after H_2 reduction and then oxidized at 773 K. Rh_2O_3 was observed as a major phase, but the peaks of Rh metal became more intensive as compared with no. 1.

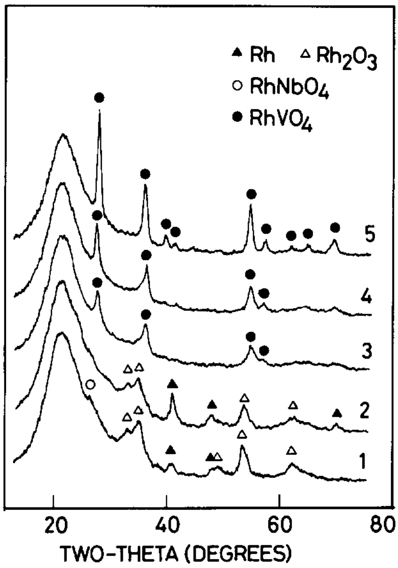

FIG. 7. X-ray diffraction patterns of the $RhNbO_4$ and $RhVO_4$/SIO-3 catalyst after the H_2 reduction followed by O_2 treatment. The $RhNbO_4$/SIO-3 catalyst was treated: (1) in H_2 at 773 K, then in O_2 at 773 K; (2) in H_2 at 773 K, then in He at 973 K and in O_2 at 773 K. The $RhVO_4$/SIO-3 catalyst was treated: (3) in H_2 at 773 K, then in O_2 at 773 K; (4) in H_2 at 773 K, then in He at 973 K and in O_2 at 773 K; (5) in H_2 at 773 K, then in He at 973 K and in O_2 at 973 K.

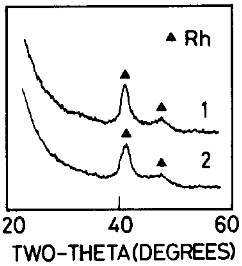

FIG. 8. Redispersion of sintered Rh particles in the vanadia-promoted Rh catalyst. The vanadia-promoted Rh catalyst in the state of Fig. 6 (no. 2) was treated: (1) in O_2 at 773 K and then in H_2 at 773 K; (2) in O_2 at 973 K and then in H_2 at 773 K.

For the vanadia-promoted Rh/SIO-3, all the intensive diffraction peaks correspond to $RhVO_4$ compound after the O_2 treatment at 773 K (no. 3). A similar result (no. 4) was obtained for the catalyst, in which the Rh particles were agglomerated to large crystallites (122 Å) by the He pretreatment at 973 K preceding the oxidation. At the higher oxidation temperature (973 K), diffraction lines of $RhVO_4$ compound became more intense (no. 5).

When the vanadia-promoted Rh catalyst in the state of Fig. 7, no. 4, was reduced in H_2 at 773 K, it gave the XRD pattern shown in Fig. 8, no. 1. All the diffraction peaks correspond to Rh metal, and the mean size of Rh particles is 57 Å. For the catalyst in the state of Fig. 7, no. 5, the XRD pattern is shown in Fig. 8, no. 2 after the H_2 reduction at 773 K. The mean size of Rh particles decreased to 40 Å. The results clearly indicate that the severely sintered Rh particles (122 Å) in the vanadia-promoted Rh catalyst can be redispersed to much smaller ones through H_2 reduction.

DISCUSSION

Formation and Agglomeration of Rhodium Compounds

For the unpromoted Rh catalyst, Rh_2O_3 particles are still dispersed well after the calcination at 773 K. Drastic crystallization is initiated at higher temperature, for instance, at 973 K (Fig. 1).

For the niobia-promoted Rh catalyst, the deposited rhodium and niobia are dispersed well or in an amorphous state at 773 K. Significant chemical reaction occurs between rhodium and niobia promoter at higher temperature (973 K), and $RhNbO_4$ compound is formed almost exclusively on silica support by the calcination at 1173 K (Fig. 2). The mean size of $RhNbO_4$ particles is about 87 Å at 973 K, and increases to 140 Å at 1173 K.

Vanadia promoter exhibits similar behaviors, but is different in its reactivity. Drastic chemical reaction and agglomeration of rhodium occurs even during the mild calcination at 773 K, giving the exclusive formation of the $RhVO_4$ compound of the particle size of 140 Å (Fig. 3). At higher temperature (973 K), the $RhVO_4$ compound agglomerates more severely, and the particle size increases to 190 Å.

The above results indicate that vanadia promoter can migrate to, and react with rhodium to form compound at much lower temperature as compared with niobia promoter. It should be also pointed out that the particle size is considerably larger in the vanadia-promoted Rh catalyst, as compared with the non- and niobia-promoted Rh catalysts. Vanadia promoter seems to exhibit high mobility on silica support due to its low melting point (963 K) and promote the agglomeration of compound, in contrast to rather difficult migration of niobia promoter, which has a higher melting point of 1793 K.

Decomposition of Compound and Redispersion of Rhodium Metal

Rhodium oxide and compounds can be decomposed by hydrogen treatment. The Rh_2O_3 particles on silica surface can be reduced completely at 373 K in hydrogen (*27*). However, higher temperature is needed for the reduction of the rhodium compound. The H_2 treatment at 473 K causes a partial reduction of the $RhVO_4$ compound, but no reduction of the $RhNbO_4$ compound. The $RhVO_4$ compound is reduced completely at 573 K in H_2, but only a part of the $RhNbO_4$ compound is reduced after the same H_2 treatment. The stability of oxides to hydrogen increases in the following order: Rh_2O_3, $RhVO_4$, and $RhNbO_4$. After the H_2 reduction of the $RhVO_4/SiO_2$ catalyst at 773 K, V_2O_3 phase is observed by X-ray diffraction by the additional treatment of the catalyst in He at higher temperature (973 K). This is in good agreement with the results of Kip *et al.* (34), in which the $RhVO_4$ compound is reduced to Rh metal and V_2O_3 according to the TPR studies. For the $RhNbO_4/SiO_2$ catalyst, NbO_2 phase is observed after the H_2 reduction at 773 K. The result supports our previous conclusion that $RhNbO_4$ compound is reduced to Rh and NbO_2 during the H_2 reduction at 773 K (*33*). From the above results, the structure change of catalysts during hydrogen treatment can be described in models as shown in Fig. 9.

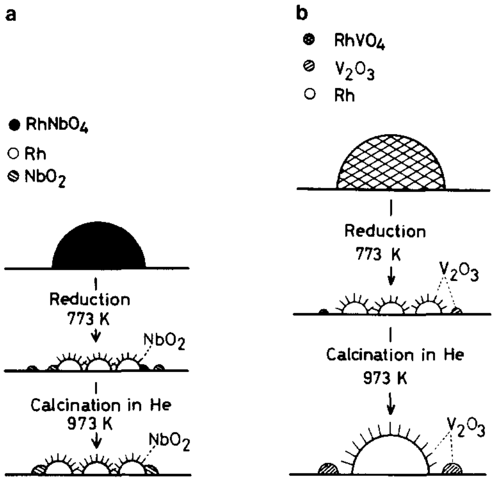

FIG. 9. A model for the behaviors of promoted Rh/SiO_2 catalysts during the treatment in H_2 and He at high temperature. (a) niobia-promoted Rh/SiO_2 catalyst, (b) vanadia-promoted Rh/SiO_2 catalyst.

The $RhNbO_4$ is reduced to Rh metal and NbO_2 in H_2 at 773 K, accompanied by splitting of the large $RhNbO_4$ particles of 140 Å into a number of smaller Rh particles of the mean sizes of 48 Å. Apparently, the redispersion is promoted by the niobia promoter, since no such redispersion occurs in the unpromoted Rh/SiO_2 catalyst. These redispersed Rh particles are also stabilized by the niobia promoter. The thermal treatment at higher temperature (973 K) following the H_2 reduction at 773 K causes almost no change in the mean size (40 Å) of Rh particles for the $RhNbO_4/SiO$-4 catalyst (Fig. 4), and only a slight increase in those of Rh particles in the $RhNbO_4/SiO$-3 catalyst (increase from 48 to 55 Å).

For the $RhVO_4/SIO$-3 catalyst, rhodium is also redispersed during the decomposition of compound. The large $RhVO_4$ particles (190 Å) split into smaller Rh particles of about 43 Å. This redispersion of Rh should be caused by the promotion effect of vanadia promoter in a way similar to that in the niobia-promoted Rh catalyst. However, it should be noted that such redispersed rhodium is not stabilized by vanadia promoter. The thermal treatment following the H_2 reduction at 773 K causes the substantial increase of the particle size of the redispersed Rh, i.e., from 43 Å to 122 Å during the He treatment at 973 K.

Both $RhNbO_4$ and $RhVO_4/SiO_2$ catalysts show similar suppression behaviors in ethane hydrogenolysis (*38*). The catalytic activities of both catalysts are suppressed by ca. 3.5 orders of magnitude after HTR relative to LTR. It is reconciled with the previous conclusion that the activity suppression for ethane hydrogenolysis is mainly caused by the geometric effects due to the decoration of Rh surface by suboxide species. Both reduced vanadia and niobia promoters seem to cover Rh surface atoms in a similar way. However, we can not exclude the possible role of the different electronic or ligand effects of these two promoters on Rh metal.

Regeneration of the Compound by Reoxidation of the Decomposed Catalysts

After the rhodium oxide and compounds are once reduced by hydrogen, thus formed Rh metal and suboxides of promoters are reoxidized in O_2. The differences between the behaviors of niobia and vanadia promoters are compared using the $RhNbO_4/SIO$-3 and $RhVO_4/SIO$-3 catalysts. For the $RhNbO_4/SIO$-3 catalyst reduced at 773 K, Rh particles (48 Å) cannot be oxidized completely by the oxygen treatment at 773 K. Only a little of $RhNbO_4$ compound is formed, and most of Rh atoms are oxidized to Rh_2O_3 (Fig. 7). For the larger Rh particles (55 Å), more Rh metal atoms remain unoxidized. However, different behaviors are observed in the reduced $RhVO_4/SIO$-3 catalyst. Almost all the Rh particles (43 Å) formed by the H_2 reduction at 773 K are oxidized to form $RhVO_4$ compound during the following oxygen treatment at 773 K (Fig. 7). It is interesting that the phenomenon is quite the same even for the large Rh crystallites (122 Å) agglomerated in the thermal treatment at high temperature (973 K), in which only the $RhVO_4$ phase is observed with the disappearance of Rh metal at 773 K in O_2 (Fig. 7, no. 4). In contrast to the incomplete oxidation of Rh metal in the niobia-promoted Rh catalyst, the oxidation of Rh metal is also promoted by the vanadia promoter. This promotion effect should be related to the high mobility of and reactivity of V_2O_5 of a very low melting point. By the calcination at 973 K, an exclusive formation of $RhVO_4$ phase is obtained on silica support (Fig. 7, no. 5).

As presented above, $RhVO_4$ particles are redispersed to small Rh particles during the decomposition process in hydrogen. Therefore, we can expect to use the vanadia promoter to redisperse the sintered Rh catalysts. In fact, the large Rh particles of about 122 Å (Fig. 6. no. 2) can be redispersed to smaller Rh particles of about 57 Å (Fig. 8, no. 1) through the calcination at 773 K, and to further smaller Rh particles of about 40 Å through the O_2 treatment at 973 K (Fig. 8, no. 2).

CONCLUSIONS

1. $RhVO_4$ compound was formed almost exclusively on silica support after the mild

calcination at 773 K. In comparison, a higher-temperature calcination at 1173 K was needed for the formation of $RhNbO_4$ compound.

2. The silica-supported $RhVO_4$ and $RhNbO_4$ catalysts exhibited significant SMSI behaviors. The capacity of H_2 chemisorption and catalytic activity for ethane hydrogenolysis were suppressed severely after the H_2 treatment at 773 K (HTR), and reversed after the O_2 treatment followed by LTR.

3. After the HTR treatment, $RhVO_4$ compound was reduced to Rh and V_2O_3, and $RhNbO_4$ reduced to Rh and NbO_2. The species of V_2O_3 and NbO_2 may cover the Rh surface to cause the suppression of chemisorption capacity and catalytic activity.

4. Rh redispersion occurred in the reduction process of the compound. By the thermal treatment in He at 973 K, the redispersed Rh particles (43 Å) in the vanadia-promoted Rh catalyst sintered severely to larger Rh particles (122 Å), while the redispersed Rh particles (40 or 48 Å) in the niobia-promoted Rh catalysts exhibited no drastic increases in their mean sizes.

5. Vanadia can be used as a promoter for the regeneration of sintered Rh catalyst. The severely sintered Rh particles (122 Å) was redispersed to a much smaller one (40 Å) through the O_2 treatment at 973 K.

ACKNOWLEDGMENTS

One of the authors (Z. Hu) thanks Tianjin University, China. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Vannice, M. A., *in* "Catalysis Vol. 3" (J. R. Anderson and M. Boudart, Eds.), p. 139. Springer-Verlag, Berlin/New York, 1982.
2. Bhasin, M. M., Bartley, W. J., Ellgen, P. C., and Wilson, T. P., *J. Catal.* **54,** 120 (1978).
3. Ichikawa, M., *J. Chem. Soc. Chem. Commun.,* 566 (1978).
4. Ichikawa, M., Fukushima, T., and Shikakura, K., *Proc. 8th Internat. Congr. Catal.* **2,** 69 (1984).
5. Kikuchi, E., Nomura, H., Matsumoto, M., and Morita, Y., *Appl. Catal.* **7,** 1 (1983).
6. Kunimori, K., Abe, H., Yamaguchi, E., Matsui, S., and Uchijima, T., *Proc. 8th Internat. Congr. Catal.* **5,** 251 (1984).
7. Vannice, M. A., *J. Catal.* **74,** 199 (1982).
8. Bracey, J. D., and Burch, R., *J. Catal.* **86,** 384 (1984).
9. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
10. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
11. Ko, E. I., and Garten, R. L., *J. Catal.* **68,** 233 (1981).
12. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
13. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 147 (1983).
14. Sadeghi, H. R., and Henrich, V. E., *J. Catal.* **87,** 279 (1984).
15. Belton, D. N., Sun, Y.-M., and White, J. M., *J. Phys. Chem.* **88,** 5172 (1984).
16. Simoens, A. J., Baker, R. T. K., Dwyer, D. J., Lund, C. R. F., and Madon, R. J., *J. Catal.* **86,** 359 (1984).
17. Chung, Y.-W., Xiong, G., and Kao, C. C., *J. Catal.* **85,** 237 (1984).
18. Takatani, S., and Chung, Y.-W., *J. Catal.* **90,** 75 (1984).
19. Belton, D. N., Sun, Y.-W., and White, J. M., *J. Amer. Chem. Soc.* **106,** 3059 (1984).
20. Ko, C. S., and Gorte, R. J., *J. Catal.* **90,** 59 (1984).
21. Raupp, G. B., and Dumesic, J. A., *J. Catal.* **95,** 587 (1985).
22. Sakellson, S., McMillan, M., and Haller, G. L., *J. Phys. Chem.* **90,** 1733 (1986).
23. Haller, G. L., and Resasco, D. E., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 36, p. 173. Academic Press, New York, 1989.
24. Singh, A. K., Pande, N. K., and Bell, A. T., *J. Catal.* **94,** 422 (1985).
25. Lin, Y.-J., Resasco, D. E., and Haller, G. L., *J. Chem. Soc. Faraday Trans. 1* **83,** 2091 (1987).
26. Kunimori, K., Doi, Y., Ito, K., and Uchijima, T., *J. Chem. Soc. Chem. Commun.,* 966 (1986).
27. Hu, Z., Nakamura, H., Kunimori, K., Asano, H., and Uchijima, T., *J. Catal.* **112,** 478 (1988).
28. Wilson, T. P., Kasai, P. H., and Ellgen, P. C., *J. Catal.* **69,** 193 (1981).
29. Ichikawa, M., Sekizawa, K., Shikakura, K., and Kawai, M., *J. Mol. Catal.* **11,** 167 (1981).
30. Mori, T., Miyamoto, A., Takahashi, N., Fukagaya, M., Hattori, T., and Murakami, Y., *J. Phys. Chem.* **90,** 5197 (1986).
31. Kip, B. J., Smeets, P. A. T., van Grondelle, J., Prins, R., *Appl. Catal.* **33,** 181 (1987).
32. Hu, Z., Nakamura, H., Kunimori, K., and Uchijima, T., *Catal. Lett.* **1,** 271 (1988).

33. Hu, Z., Nakamura, H., Kunimori, K., Yokoyama, Y., Asano, H., Soma, M., and Uchijima, T., *J. Catal.* **119,** 33 (1989).

34. Kip, B. J., Smeets, P. A. T., van Wolput, J. H. M. C., Zandbergen, H. W., van Grondelle, J., and Prins, R., *Appl. Catal.* **33,** 157 (1987).

35. Murakami, Y., *in* "Preparation of Catalyst III" (G. Poncelet, P., Grange, and P. A. Jacobs, Eds.), p. 775. Elsevier, Amsterdam, 1983.

36. Lee, C., and Schmidt, L. D., *J. Catal.* **101,** 123 (1986).

37. Shaplygin, I. S., Prosychev, I. I., and Lazarev, V. B., *Russ. J. Inorg. Chem. Eng. Transl.* **23,** 773 (1973).

38. Kunimori, K., Hu, Z., Nakamura, H., Wakasugi, T., Yamakawa, F., and Uchijima, T., *Shokubai* **31,** 60 (1989); *in* "63rd CATSJ Meeting Abstract No. A4 (1989)."