JOURNAL OF CATALYSIS 119, 33–46 (1989)

Structural Transformation in Nb_2O_5-Promoted Rh Catalysts during Calcination and Reduction Treatments

Z. HU, H. NAKAMURA, K. KUNIMORI,[1] Y. YOKOYAMA,[2] H. ASANO, M. SOMA,* AND T. UCHIJIMA[1]

*Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan, and *National Institute for Environmental Studies, Tsukuba, Ibaraki 305, Japan*

Received November 30, 1988; revised March 1, 1989

The extent of Rh–Nb_2O_5 interaction in the niobia-promoted Rh/SiO_2 catalyst depends on parameters such as calcination temperature. For the Nb_2O_5-promoted Rh/SiO_2 catalyst with the Nb/Rh atomic ratio of unity, no significant SMSI effects were observed after air calcination at 773 K. However, this catalyst exhibits significant SMSI behaviors after calcination at higher temperatures (973 and 1173 K). After high-temperature reduction at 773 K, the capacity of H_2 chemisorption typically diminished almost to zero and the catalytic activity for ethane hydrogenolysis was suppressed by ca. 3.5 orders of magnitude compared with that after low-temperature reduction at 373 K. X-ray diffraction showed that the $RhNbO_4$ compound was formed, with the amount increasing with increasing calcination temperature. After air calcination at 1173 K, the $RhNbO_4$ compound was formed almost exclusively on the SiO_2 surface. The $RhNbO_4$ compound was reduced to Rh and NbO_2 during HTR treatment at 773 K, accompanied by splitting of the large $RhNbO_4$ particle into a number of smaller Rh particles. The mechanism of Rh–Nb_2O_5 interaction is discussed. It is proposed that the NbO_2 species formed during the HTR treatment block surface Rh atoms to induce strong Rh–Nb_2O_5 interaction (SMSI).

INTRODUCTION

There has been much interest in the strong metal–support interaction (SMSI) as well as in the effect of oxide promoter in supported metal catalysts (*1–6*). The metal–oxide interaction modifies the catalytic properties of the metal significantly (*7–11*). Evidence for a strong metal–support interaction has been observed in TiO_2-promoted Rh catalysts (*12*) and in Nb_2O_5-promoted Ni catalyst (*13*). Such oxide promoters have also been reported to modify substantially the catalytic properties of the metal (*5–7*). Kunimori *et al.* reported that a Nb_2O_5-promoted Rh/SiO_2 catalyst exhibited SMSI behavior in ethane hydrogenolysis reaction, the Rh–Nb_2O_5 interaction being as strong as that in the Rh/Nb_2O_5 catalysts (*14*). The results show that metal–support and metal–oxide promoter interactions are quite similar.

Metal–oxide interaction was discovered many years ago, and the early literature has been reviewed by Solymosi and Schwab (*15, 16*). Tauster and co-workers first reported SMSI phenomena (*17, 18*). This work has led to numerous studies on the interesting properties of many transition metals supported on reducible oxides. The studies have enhanced our understanding of the mechanism of the strong metal–support interaction (*19–29*). In a current model of SMSI, a reduced oxide species is formed during high-temperature reduction (HTR) and then blocks surface metal atoms, leading to a suppression in the capacity of H_2 chemisorption and in the catalytic activity for ethane hydrogenolysis reaction ("decoration model") (*20, 30*). However, the structure of the reduced oxide species and their interaction with metal still remain unclear.

[1] To whom correspondence should be addressed.

[2] Present address: Corporate Research and Development Laboratory, Toa Nenryo Kogyo K. K., Ohimachi, Iruma, Saitama 354, Japan.

0021-9517/89 $3.00

The term "SMSI behavior" is used in this paper for the cases which meet the definition in the original observations (*17, 18*), i.e., a drastic suppression of chemisorption ability and/or catalytic activity after high-temperature reduction and its recovery after high-temperature O_2 treatment followed by low-temperature reduction (LTR). SMSI behavior has been amply confirmed in the originally reported catalyst systems (metal/TiO_2, metal/Nb_2O_5, etc.), and new catalyst systems (TiO_2-, V_2O_3-, and Nb_2O_5-promoted metal catalysts) have been observed to exhibit equivalent behavior (*4, 12, 13, 29*). Because the amount of the reducible oxide is significantly smaller in the latter catalyst systems, we may be able to obtain clearer information about the structure of the oxide which interacts strongly with metal. For the promoted metal catalysts, mixed oxide may be formed between metal and oxide promoter. This chemistry will affect the degree of metal–oxide interaction. Formation of the $RhVO_4$ mixed oxide has been proposed in V_2O_5-promoted Rh catalysts by Kip *et al.* (*31*). They found that vanadium oxide hampers the reduction of rhodium oxide in $Rh/V_2O_5/SiO_2$ catalysts, which do not contain "free" V_2O_5 when the ratio of V/Rh is 0.9. In the preceding papers (*32, 33*), we have found a formation of $RhNbO_4$ as a new phase by X-ray diffraction during calcination of the Nb_2O_5-promoted Rh/SiO_2 catalyst. It has also been suggested that the Nb_2O_5 on the SiO_2 surface migrates toward the rhodium particle during the calcination process to form the $RhNbO_4$ compound. Such Nb_2O_5 or $RhNbO_4$ is reduced during high-temperature reduction, and spreads on the surface of Rh particles, leading to the suppression of H_2 chemisorption capacity and ethane hydrogenolysis activity. Significant SMSI effects have been observed in the Nb_2O_5-promoted 0.5% Rh/SiO_2 (Nb/Rh = 9.3) and Nb_2O_5-promoted 5% Rh/SiO_2 (Nb/Rh = 3.1) catalysts (*32*). Because these catalysts contain an excess amount of Nb_2O_5 promoter, a large part of which does not interact directly with rhodium, little information about the structure of reduced niobia species and its interaction with Rh have been obtained so far. Thus, an attempt to use a Nb_2O_5-promoted Rh/SiO_2 catalysts with the Nb/Rh atomic ratio of unity might help us to understand in detail the migration and reduction behavior of rhodium and niobia promoter on the silica surface.

In this paper, the results of our recent work using Nb_2O_5-promoted Rh catalysts (Nb/Rh = 1.0) and $RhNbO_4/SiO_2$ catalysts as starting materials will be presented. TPR, TPO, and XPS experiments were carried out to characterize the Rh–Nb_2O_5 interaction. The structure change of the catalyst was studied by X-ray diffraction. The catalytic properties and the characterization results will be described first, followed by a discussion of the mechanism of Rh–Nb_2O_5 interaction and the structure of the reduced niobia species in the SMSI state.

EXPERIMENTAL

Preparation of catalyst. A silica of Japan reference catalyst (JRC-SIO-3, BET surface area of 186 m^2/g) was used as support (*34*). After calcination in air at 773 K, the SiO_2 support was impregnated with a mixed aqueous solution of $RhCl_3$ and $(NH_4)_3[NbO(C_2O_4)_3]$, and then dried at 393 K overnight. Catalysts A and B were obtained by calcining this impregnated sample in air at 773 K for 1 h and at 973 K for 3 h. Rhodium content was 4.8 wt%. For catalyst C, the SiO_2 support was 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. A 4.2 wt% Rh/SiO_2 catalyst was prepared by impregnation of the precalcined silica with a solution of $RhCl_3$, then dried at 393 K but not calcined. This sample was then impregnated with $(NH_4)_3[NbO(C_2O_4)_3]$ dissolved in deionized water. Catalyst C was obtained by calcining this sample in air at 1173 K for 3 h after it had been dried at 393 K overnight. For all

the catalysts, the Nb_2O_5 loading was chosen so that the atomic ratio of Nb/Rh is unity.

H_2 chemisorption. Volumetric H_2 chemisorption was measured in a conventional glass vacuum system, as described in (*35*). The catalyst was pretreated in O_2 at 773 K for 1 h, followed by low-temperature reduction at 373 K 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 at the catalyst reduction temperature for 1 h.

O_2 consumption. The O_2 consumption was studied in the same glass vacuum system. After the measurement of H_2 adsorption, the catalyst was evacuated at 773 K for 1 h to remove possible H_2 adsorbate on the catalyst. After the admission of O_2, the catalyst was heated at 773 or 873 K. The O_2 uptake was instantaneous; it was followed by a gradual change, the rate of which became negligible after 1–2 h. Therefore, the amount of O_2 consumption was measured after being heated at 773 for 3 h or at 873 K for 1.5 h.

Ethane hydrogenolysis. The catalytic activity measurements for the ethane hydrogenolysis reaction were performed in a microcatalytic pulse reactor (*36*). The details of the procedure have been described elsewhere (*32*). The reaction was carried out after the catalyst was pretreated in O_2 at 673 K, followed by low-temperature reduction at 373 K or high-temperature reduction at 773 K.

X-ray diffraction (XRD). 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 made available the precise determination of d spacing values of diffraction lines. For normal measurements (continuous scan), slower scan speed (0.5°/min) was used. For step scan measurements, a scan step of 0.04° and a preset time of 20 s were employed.

X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using a VG ESCA LAB-5 spectrometer equipped with both Al$K\alpha$ and Mg$K\alpha$ X-ray sources, a preparation chamber, and signal averager (*35*). The signal of Si 2p at 103.3 eV was used as a standard for the evaluation of core-electron binding energies.

Temperature-programmed reduction (TPR). The TPR measurements were performed in a flow system with the catalyst (0.25 g) placed in a microreactor connected to a quadrupole mass spectrometer, as described previously (*32*). After the catalyst was calcined in O_2 flow at 773 K for 1 h, it was purged with He gas at 773 K to remove any possible oxygen adsorbate over the support. The catalyst was subsequently cooled in He to room temperature; then a mixture of 1.04% H_2–He was passed through the catalyst bed at 30 cm^3/min, and the H_2 consumption was monitored as the catalyst temperature was raised at 5 K/min up to 973 K.

Temperature-programmed oxidation (TPO). TPO measurements were carried out in the same flow system. After the catalyst (0.25 g) was reduced at the desired temperture, it was purged with He purified at liquid nitrogen temperature by raising the temperature to 973 K to remove H_2 adsorbate on the catalyst. The sample was subsequently cooled in He to room temperature; then a mixture of 0.105% O_2–He was passed through the catalyst bed at 30 cm^3/min, and the O_2 consumption was monitored as the catalyst temperature was raised at 10 K/min to 973 K.

RESULTS

The catalytic properties of the Nb_2O_5-promoted Rh catalysts are presented in Table 1. The fresh catalyst was first reduced in H_2 at 773 K (HTR) before any adsorption or activity measurements. As will be presented later, this first HTR treatment was performed to decompose the $RhNbO_4$ compound. It can thus be considered that the obtained chemisorption capacities and ac-

TABLE 1

Catalytic Properties of Nb_2O_5-Promoted Rh/SiO_2 Catalysts

Catalyst	H/Rh[a]		Extent of activity suppression[b]	Rh particles[c]	
	LTR	HTR		Mean size (Å)	Dispersion
Catalyst A	0.061	0.020	1	43	0.21
Catalyst B	0.053	0.003	$10^{-3.5}$	85	0.11
Catalyst C	0.130	0.004	$10^{-3.5}$	48	0.19

[a] The fresh catalyst was first reduced in H_2 at 773 K (1st HTR) before the chemisorption and activity measurements. Chemisorption capacities were measured after high-temperature reduction at 773 K (HTR) and O_2 treatment at 773 K followed by low-temperature reduction at 373 K (LTR).

[b] The extent of activity suppression is given as a ratio of the catalytic activity for ethane hydrogenolysis after HTR treatment at 773 K to that after LTR treatment at 373 K (r_{HTR}/r_{LTR}).

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

tivities are the catalytic properties of the Rh particles. For catalyst A (calcined at 773 K), almost the same catalytic activities were observed after LTR at 373 K and HTR at 773 K. However, significant suppression effects were observed in catalysts B and C, which were calcined in air at higher temperatures (973 and 1173 K, respectively). After the O_2 treatment followed by LTR, the catalytic activity of catalyst B increased by ca. 3.5 orders of magnitude relative to that after the first HTR treatment. For catalyst C, the observed suppression extent was almost the same as that in catalyst B. The suppression was reversible. Following the first HTR treatment, the catalytic activity of catalyst C increased (by ca. 3.2 orders of magnitude) after the O_2 treatment at 673 K followed by LTR treatment. This activity decreased (by ca. 3.5 orders) again after the following HTR treatment. Almost the same suppression extents were observed after the first and second HTR treatments (*39*).

The results of H_2 chemisorption and XRD studies are also shown in Table 1. The H/Rh values from H_2 chemisorption measurements are less than those Rh dispersions obtained by X-ray diffraction. This result suggests that the Rh particles are partially covered with the Nb_2O_5 promoter even after LTR, as reported previously (*32*). The mean size of Rh particles is different for the Nb_2O_5-promoted Rh catalysts calcined at different temperatures. The size is 43 Å for catalyst A. This size increased to 85 Å after the catalyst was calcined at higher temperature (catalyst B). However, the particle size decreased to 48 Å in catalyst C, even though the catalyst was calcined at much higher temperature (1173 K). It is interesting that the mean size of Rh particles of catalyst C is smaller than that of catalyst B.

The H_2 chemisorption capacity decreased with increasing catalyst reduction temperature. In catalyst A, substantial H_2 chemisorption (about one-third of the value after LTR at 373 K) was observed even after HTR at 773 K. However, the capacity of H_2 chemisorption diminished almost to zero in catalysts B and C. Apparently, the Nb_2O_5-promoted Rh catalysts more or less show the behaviors characteristic of SMSI phenomena in H_2 chemisorption and ethane hydrogenolysis reaction, because both the chemisorption capacities and the catalytic activities decrease with increasing catalyst reduction temperature. As suggested by the decoration model of SMSI, the suppression effects are due to the blockage of surface Rh atoms. It thus can be considered that in catalyst A only part of the Rh interacts with the niobia promoter, but almost all of the surface Rh atoms are blocked by the niobia promoter in catalysts B and C after HTR. The different extent of SMSI in catalysts A and B supports our previous conclusion that the extent of $Rh–Nb_2O_5$ interaction is increased by calcining the Nb_2O_5-promoted Rh catalyst in air at higher temperature (*32*).

In order to characterize the structure of rhodium and niobia promoter, X-ray diffraction patterns were recorded after the catalysts were treated in H_2 or O_2 at different temperatures. For catalyst A, which was calcined in air at 773 K, only a few broad diffraction peaks were observed, which can be attributed to Rh_2O_3 (Fig. 1,

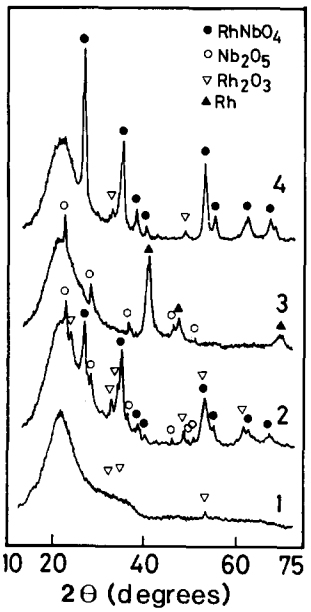

FIG. 1. X-ray diffraction patterns of Nb_2O_5-promoted Rh catalysts calcined at different temperatures. (1) Catalyst A (calcined in air at 773 K). (2) Catalyst B (calcined in air at 973 K). (3) Catalyst B after being reduced in H_2 at 773 K. (4) Catalyst B after being calcined in air at 1173 K.

No. 1). It suggests that Nb_2O_5 is dispersed well or amorphously. However, the diffraction pattern of catalyst B calcined at 973 K is more complex. As shown in Fig. 1 (No. 2), three phases (Rh_2O_3, Nb_2O_5, and $RhNbO_4$) are observed. A new phase of $RhNbO_4$ compound was formed between Rh and Nb_2O_5 promoter. The XRD pattern of catalyst B after H_2 reduction at 773 K is also presented in Fig. 1 (No. 3). The diffraction peaks of the Rh metal are observed with the disappearance of the $RhNbO_4$ phase. However, it should be noted that no reduction was observed in the intensities of the diffraction peaks of the Nb_2O_5 phase (Nos. 2 and 3).

Catalyst B was further calcined at a higher temperature (1173 K). The XRD pattern is shown in Fig. 1, No. 4. The intensities of the diffraction peaks of the $RhNbO_4$ compound increased substantially. At the same time, the diffraction peaks of the Nb_2O_5 phase disappeared in the XRD pattern (No. 4), implying that a reaction occurred between rhodium and the niobia promoter:

$$Rh_2O_3 + Nb_2O_5 \rightarrow 2RhNbO_4$$

The Rietveld analysis of X-ray powder diffraction data was carried out in order to reconfirm the previous assignment (*32*). Figure 2 illustrates the profile fit and the difference patterns for catalyst B after calcination at 1173 K. Crosses are observed intensities, the solid line overlying them is the calculated intensity, and Δy_i is the difference between observed and calculated intensities. The short vertical lines mark the positions of possible Bragg peaks of the $RhNbO_4$ compound. The observed XRD pattern contains the $RhNbO_4$ compound almost exclusively with a little of the Rh_2O_3 phase. Figure 2 shows that the calculated pattern fits the observed one well. The tetragonal lattice parameters of the $RhNbO_4$ compound were refined to be $a = 4.708$ Å, $c = 3.017$ Å. This result is also in reasonable agreement with those of $RhNbO_4$ powders ($a = 4.685$ Å, $c = 2.980$ Å) by Shaplygin *et al.* (*37*).

In catalyst C, the silica support precalcined at 1173 K was used and calcined finally at the same temperature after its preparation. The XRD patterns of catalyst C are shown in Fig. 3 (No. 1). All the diffraction peaks correspond to the $RhNbO_4$ phase, except for a small peak due to the Rh_2O_3 phase. No peaks corresponding to the Nb_2O_5 oxide are observed. The pattern is in good agreement with that of catalyst B calcined at 1173 K (Fig. 1, No. 4). Therefore, the $RhNbO_4$ compound has been formed almost exclusively on the SiO_2 surface by the high-temperature calcination at 1173 K. After the H_2 reduction at 473 K, the small Rh_2O_3 peak disappeared with the appearance of a small Rh metal peak (No. 2).

The structure changes of the $RhNbO_4$ phase are presented by XRD patterns in Fig. 4 after H_2 or O_2 treatments. Curve 1 is the XRD pattern of catalyst C after H_2 reduction at 773 K, where the diffraction

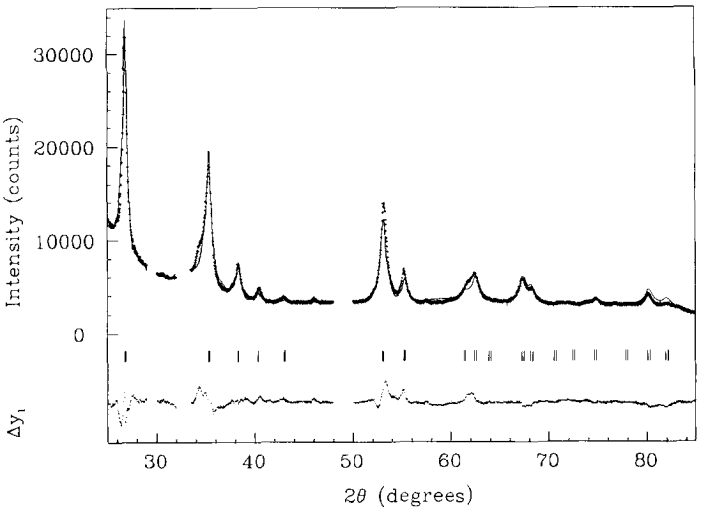

FIG. 2. Rietveld refinement patterns for the $RhNbO_4$ compound in catalyst B after being calcined at 1173 K.

peaks of the $RhNbO_4$ phase disappeared, and only the main diffraction peak (111) of the Rh metal appeared, but almost no other peaks of the Rh phase were observed. A small peak around 26.0° was observed, and its *d* spacing value (3.421 Å) is the same as that of the most intensive diffraction line (400) of the NbO_2 phase (3.42 Å). This diffraction peak can be distinguished significantly from the most intensive (110) peak of $RhNbO_4$ (3.321 Å) or other phases such as Nb_2O_5, Rh_2O_3, etc. After catalyst C was

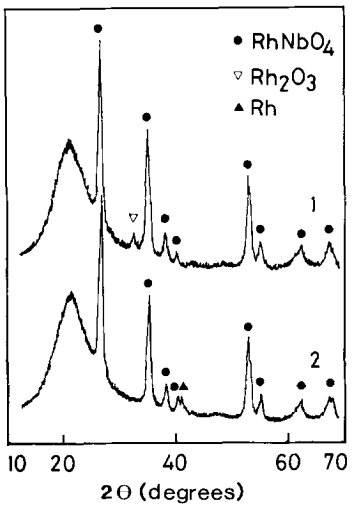

FIG. 3. X-ray diffraction patterns of catalyst C. (1) Catalyst C (calcined in air at 1173 K). (2) After step 1, the catalyst was reduced in H_2 at 473 K.

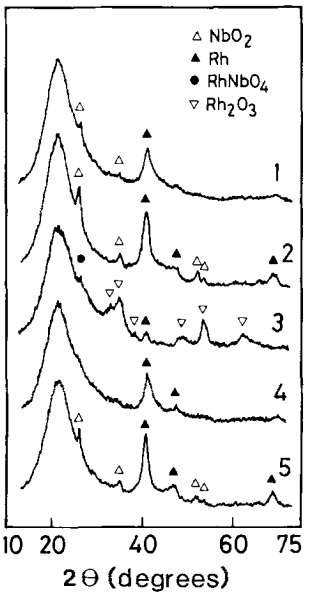

FIG. 4. X-ray diffraction patterns of catalyst C after being treated in H_2 or O_2. (1) Catalyst C reduced in H_2 at 773 K. (2) After step 1, the catalyst was treated in He at 973 K. (3) After step 1, the catalyst was calcined in air at 773 K. (4) After step 3, the catalyst was reduced in H_2 at 773 K. (5) After step 4, the catalyst was treated in He at 973 K.

calcined in He at 973 K following reduction at 773 K, the diffraction pattern of this phase became more clear (No. 2). A best-fit was obtained if we calculate the d spacing values by assuming the tetragonal NbO_2 structure (a = 13.71 Å, c = 5.985 Å). We can thus conclude that the $RhNbO_4$ compound is reduced to the Rh metal, accompanied with the formation of reduced niobia species (NbO_2).

O_2 treatment at 773 K has always been used to restore the normal state from SMSI. The XRD pattern after calcination in air at 773 K is shown in No. 3. The main peaks correspond to the Rh_2O_3 phase. The diffraction peaks of the NbO_2 phase disappeared, probably as a consequence of oxidation to Nb_2O_5. A small diffraction peak of the Rh metal was still observed (No. 3). It indicates that the calcination treatment at 773 K is not sufficient to oxidize the Rh particles completely.

High-temperature reduction treatment can induce SMSI again after restoration by O_2 treatment. The XRD pattern after the HTR treatment at 773 K is shown in Fig. 4 (No. 4). Only the Rh phase was observed. The XRD pattern is similar to that after the first HTR treatment (No. 1), except for the absence of the NbO_2 diffraction peak at 26°. XRD pattern No. 5 was obtained after thermal treatment in He at 973 K following the second HTR treatment. The diffraction peaks of the Rh metal became sharper, indicating some agglomeration of Rh particles during the He treatment at 973 K. The diffraction peaks of NbO_2 were also observed in pattern No. 5, although the intensity was less than that in pattern No. 2. It should be pointed out that no NbO_2 phase was observed even after the same He thermal treatment when the catalyst was reduced at 473 K. Therefore, it can be considered that He treatment at 973 K mainly caused the highly dispersed NbO_2 to agglomerate to large crystallines.

X-ray photoelectron spectroscopy was used to characterize the Rh catalysts in the oxidized state. The binding energies of Rh $3d_{5/2}$ are presented in Table 2. For the nonpromoted Rh/SiO_2 catalyst which was calcined in air at 973 K, the Rh $3d_{5/2}$ binding energy is 308.1 eV. In catalyst C calcined at 1173 K, the Rh $3d_{5/2}$ binding energy is 309.1 eV. From the results of X-ray diffraction, the main phase is Rh_2O_3 in the nonpromoted Rh catalyst, and $RhNbO_4$ in catalyst C after these treatments. It can thus be concluded that the Rh $3d_{5/2}$ binding energies are 308.1 eV for Rh_2O_3 and 309.1 eV for $RhNbO_4$ particles on the SiO_2 surface. Therefore, the formation of mixed oxide with Nb_2O_5 induces a shift in the Rh $3d_{5/2}$ binding energies to the higher energy side. After the $RhNbO_4$ has been once reduced and then treated in O_2 at 773 K, the observed Rh $3d_{5/2}$ binding energy is 308.2 eV, which coincides quite well with that in the Rh_2O_3 phase. The results should be compared with the observation by X-ray diffraction which shows the coexistence of Rh_2O_3 and Rh as the main phases. However, no Rh metal was detected by XPS. This difference between XRD and XPS leads to the interpretation that the O_2 treatment at 773 K causes the oxidation of the outer layer of the Rh particles to Rh_2O_3, with the Rh core still unchanged. For catalyst B, which was calcined in air at 973 K, the observed Rh $3d_{5/2}$ binding energy is 308.9 eV, in reasonable agreement with that of the $RhNbO_4$ compound. However, the result of X-ray diffraction shows that the catalyst contains two kind of rhodium:

TABLE 2

Binding Energies of Rh $3d_{5/2}$ in Nb_2O_5-Promoted Rh Catalysts

Catalyst	Calcination temperature (K)	Binding energy of Rh $3d_{5/2}$ (eV)
Catalyst C	1173	309.1
Catalyst C[a]	773	308.2
Catalyst B	973	308.9
5 wt% Rh/SiO_2	973	308.1

[a] After catalyst C had been reduced in H_2 at 773 K, it was calcined in O_2 at 773 K.

Rh_2O_3 and $RhNbO_4$. No significant contribution of Rh_2O_3 was observed by XPS. This can lead to the interpretation that calcination results in the formation of the $RhNbO_4$ compound on the surface layer of Rh_2O_3 particles.

Temperature-programmed reduction was used to study the interaction between rhodium and the niobia promoter in the oxide state. Figure 5 shows the TPR spectra of catalyst C. By calcination in air at 1173 K, the reduction peak shifted significantly to the higher temperature side (Fig. 5, No. 1), considering that the observed reduction temperature of Rh_2O_3 was about 350 K for the nonpromoted Rh/SiO_2 catalysts (*32*). The H_2 consumption has a maximum around 800 K. A small reduction peak around 440 K was also observed at the lower temperature side. The calcination of the catalyst in O_2 at 773 K after H_2 reduction at 773 K gives the TPR profile No. 2 shown in Fig. 5. H_2 consumption is observed mainly around 350–580 K, with a broad tail up to 870 K. As also discussed in a previous paper (*32*), the reduction peak at higher temperatures (about 800 K) can be attributed to the crystallized $RhNbO_4$ compound (No. 1). Thus, the H_2 consumption at the tailing part to 873 K in profile No. 2 may correspond to the reduction of the $RhNbO_4$ precursor (surface compound) (*32*). The H_2 consumption at the lower temperature side is due to the reduction of Rh_2O_3 oxide, although its reduction temperature could have shifted to higher temperatures by interaction with the Nb_2O_5 promoter. The XRD results also support such interpretations, in which the main phase is assigned to $RhNbO_4$ in TPR profile No. 1, and to Rh_2O_3 in TPR profile No. 2.

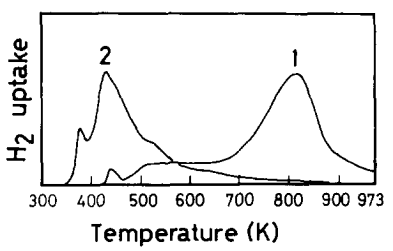

FIG. 5. TPR spectra of catalyst C. (1) Catalyst C calcined in air at 1173 K. (2) Following the H_2 reduction at 773 K, catalyst C was calcined in O_2 at 773 K.

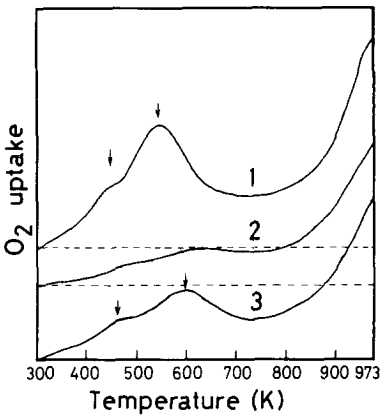

FIG. 6. TPO spectra of catalyst C. (1) Catalyst C after being reduced in H_2 at 773 K. (2) Following H_2 reduction at 773 K, catalyst C was calcined in O_2 at 773 K and reduced in H_2 at 473 K. (3) Following H_2 reduction at 773 K, catalyst C was calcined in O_2 at 773 K and reduced again in H_2 at 773 K.

In order to obtain more information about the structure of the reduced niobia species, temperature-programmed oxidation spectra were measured. The TPO profile of catalyst C ($RhNbO_4/SiO_2$) after reduction at 773 K is presented in Fig. 6 (No. 1). The O_2 consumption has a maximum around 540 K and another maximum at temperatures higher than 973 K. Because of the large Rh particle size of the catalyst and the low O_2 concentration (0.105% O_2) used in TPO measurements, higher temperatures are needed for complete oxidation. The O_2 consumption peak at the higher temperature side can be considered the oxidation of the bulk Rh metal. The $RhNbO_4$ compound was reduced in H_2 at 773 K and then calcined in O_2 at 773 K. The TPO profile No. 2 is observed as shown in Fig. 6, after the H_2 reduction at 473 K for this catalyst. The O_2 consumption peak at the higher temperature side remained almost unchanged, but the amount of O_2 consumption at the lower temperature side decreased substantially. In Fig. 6 (No. 3), the TPO

profile is presented after the second HTR treatment at 773 K. The O_2 consumption increased at the lower temperature side, compared with No. 2. In contrast to the first HTR (Fig. 6, No. 1), however, a significant decrease was observed in the amount of O_2 consumption at the lower temperature side. As will be discussed later, the oxidation peak at the lower temperture side can be attributed to the oxidation of the reduced niobia species.

O_2 consumption was studied by a static vacuum system to estimate the amount of reduced niobia species. For the complete oxidation of Rh metal,

$$2\ Rh + \tfrac{3}{2}O_2 \rightarrow Rh_2O_3,$$

the amount of O_2 consumption is 1.5 in O/Rh value. For the Nb_2O_5-promoted Rh/SiO_2 catalysts evacuated at high temperature (773 K) after reduction, oxygen is consumed mainly for the oxidation of Rh metal and reduced niobia species. The part of O_2 consumption exceeding 1.5 in O/Rh value should be attributed to the oxidation of reduced niobia species.

The results are presented in O/Rh values in Table 3. In the second column are shown the values of O_2 consumption after the H_2 reduction at 473 K for the catalyst which experienced first HTR followed by oxidation at 773 or 873 K. For catalyst A, the amount of O_2 consumption is 1.45 in O/Rh value after H_2 reduction at 473 K. This value is in reasonable agreement with that for complete oxidation of the Rh metal. In catalyst C, the amount of O_2 consumed during the thermal treatment at 773 K is 1.12 in O/Rh value after H_2 reduction at 473 K. When the thermal treatment was carried out in O_2 at 873 K, the observed O_2 consumption increased to 1.42 in O/Rh value. The above results suggest that the thermal treatment at 773 K is sufficient to oxidize Rh particles in catalyst A, but a higher temperature (873 K) is needed for catalyst C.

TABLE 3

Amount of O_2 Consumption for Nb_2O_5-Promoted Rh Catalyst

Catalyst	O_2 consumption (O/Rh)[a] after H_2 treatments at varying temperatures			
	(1) 1st HTR	(2) 473 K	(3) 573 K	(4) 2nd HTR
Catalyst A[b]	1.60	1.45	—	1.59
Catalyst C[c]	2.02	1.42	1.50	1.66
Catalyst C[b]	1.91	1.12	1.31	1.56

[a] The O_2 consumption measurements were made according to the following sequence: (1) 1st HTR at 773 K, (2) H_2 reduction at 473 K, (3) H_2 reduction at 573 K, and (4) 2nd HTR at 773 K.

[b] The amount of O_2 consumed during thermal treatment at 773 K.

[c] The O_2 consumption during thermal treatment at 873 K.

After the first HTR treatment at 773 K, the amount of O_2 consumed by catalyst A is 1.60 in O/Rh value. It implies that some reduced niobia species have been formed with the amount of about 0.1 in O/Rh value. Almost the same O_2 consumption was observed after the first and the second HTR treatment at 773 K in catalyst A.

For catalyst C, the data for both thermal treatments at 773 and 873 K are presented in Table 3 for comparison. In all cases, the O_2 consumption values during thermal treatment at 773 K are less than those at 873 K. As discussed above, it is more appropriate to estimate the amount of reduced niobia species from the data at 873 K. The amount of O_2 consumption is 2.02 in O/Rh value after the first HTR at 773 K. This value is significantly higher than those of any of the successive reduction treatments. The result indicates that some irreversible change occurred in catalyst C. Following the first HTR at 773 K, the O_2 consumption is 1.42 after H_2 reduction at 473 K. This value increased to 1.66 after the second HTR at 773 K. The O_2 consumption increased with increasing catalyst reduction temperature, implying that more Nb_2O_5 promoter was reduced by H_2 reduction at a higher temperature. The amount of reduced niobia species was about 0.52 in O/Rh value

after the first HTR at 773 K, but decreased to 0.16 after the second HTR at the same temperature. It should be pointed out that no significant O_2 consumption was observed in the Nb_2O_5/SiO_2 catalyst system after the same HTR treatment.

DISCUSSION

In Nb_2O_5-promoted Rh/SiO_2 catalysts, the migration behaviors of Rh and Nb_2O_5 particles depend on the calcination temperatures of the impregnated precursors on the silica surface. From the results obtained by X-ray diffraction (Fig. 1), the structure of the Nb_2O_5-promoted Rh/SiO_2 catalysts calcined at different temperatures can be described by a model as shown in Fig. 7.

During calcination at 773 K, the precursors decompose to rhodium and niobium oxides. The Nb_2O_5 is well dispersed, and most of the niobia particles may be located apart from Rh_2O_3 particles on the silica surface (catalyst A). Most of such separated niobia particles are hardly reduced even by HTR treatment. Those Nb_2O_5 promoter particles which are present in the vicinity of rhodium particles may be reduced in HTR

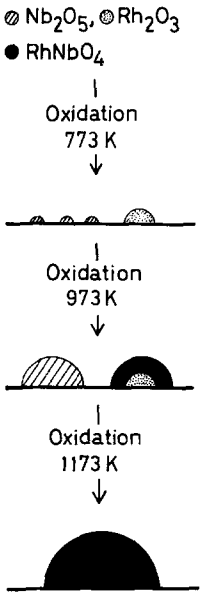

FIG. 7. Model for the formation of the $RhNbO_4$ compound during the calcination process.

treatment. However, the amount is limited (0.1 in O/Rh value). The reduced niobia species block some of the surface Rh atoms to cause the decrease in H_2 chemisorption capacity, but not sufficiently to induce strong $Rh–Nb_2O_5$ interaction, since no significant suppression was observed in the catalytic activity for the ethane hydrogenolysis reaction.

The particles of rhodium and niobium oxide are movable during calcination at higher temperatures. The calcination treatment at 973 K leads to a formation of three phases (Nb_2O_5, Rh_2O_3, and $RhNbO_4$) on the silica surface. During the calcination process, some of the Nb_2O_5 particles migrate toward the Rh_2O_3 particles and form a surface layer of $RhNbO_4$ compound on them. The other Nb_2O_5 particles agglomerated to larger ones (catalyst B) to form crystalline Nb_2O_5. In this catalyst, the significant SMSI effects (H/Rh diminished to zero and ethane hydrogenolysis activity suppressed by ca. 3.5 orders of magnitude) were observed after HTR treatment. The reduced niobia species may be formed from reduction of the $RhNbO_4$ compound (*32, 33*). However, those Nb_2O_5 particles which are located apart from the rhodium particles would not be reduced even by HTR treatment at 773 K. In practice, no reduction of Nb_2O_5 oxide was observed by X-ray diffraction (Fig. 1, No. 3). The results indicate that the niobia species with its amount less than that of the total Rh atoms is sufficient to induce strong $Rh–Nb_2O_5$ interaction.

During high-temperature calcination at 1173 K, the larger particles of Nb_2O_5 and Rh_2O_3 are also movable. As a consequence of the reaction between rhodium and niobium oxide, almost a single phase of $RhNbO_4$ was formed on the silica surface, accompanied by the disappearance of the Nb_2O_5 and Rh_2O_3 phases (catalyst C and catalyst B calcined at 1173 K). The high-temperature calcination caused significant sintering of particles, as indicated by the sharp diffraction peaks of the $RhNbO_4$ compound.

In catalyst C, the $RhNbO_4$ compound was formed almost exclusively on the silica surface. As indicated by the TPR spectra, the $RhNbO_4$ compound was reduced at much higher temperatures compared with Rh_2O_3. This compound can be reduced completely by HTR at 773 K. Significant SMSI effects were observed in this $RhNbO_4/SiO_2$ catalyst. After HTR treatment at 773 K, the capacity of H_2 chemisorption diminished to zero, and the catalytic activity for ethane hydrogenolysis was suppressed by ca. 3.5 orders of magnitude compared with that after the following LTR treatment (*39*). From the comparison of catalyst A with catalyst B or C, severe suppression of catalytic activity for ethane hydrogenolysis was observed only after the H/Rh value diminished almost to zero (*32*). The results suggest that a nearly complete blockage of the Rh surface is required for a large SMSI effect.

This $RhNbO_4/SiO_2$ catalyst system was used to characterize the Rh–Nb_2O_5 interaction. After the first HTR treatment at 773 K, the NbO_2 phase was identified by X-ray diffraction (Fig. 4, Nos. 1 and 2). The results indicate clearly that NbO_2 is a reduction product of the $RhNbO_4$ compound. The amount of O_2 consumed by the oxidation of the reduced niobia species is 0.52 in O/Rh value after HTR treatment of the $RhNbO_4/SiO_2$ catalyst at 773 K. This amount is in good agreement with 0.5 in O/Rh value which is predicted from the oxidation of NbO_2 to Nb_2O_5,

$$2NbO_2 + \tfrac{1}{2}O_2 \rightarrow Nb_2O_5.$$

Therefore, the stoichiometry of the reduction of the $RhNbO_4$ compound by H_2 can be written as

$$RhNbO_4 + 2H_2 \rightarrow Rh + NbO_2 + 2H_2O.$$

The $RhNbO_4$ compound is reduced easily in comparison with Nb_2O_5. In catalyst B, no reduction of those Nb_2O_5 particles was observed even after the same HTR treatment, as indicated by X-ray diffraction (Fig. 1, No. 3). Since significant SMSI effects were observed in this $RhNbO_4/SiO_2$ catalyst after H_2 reduction at 773 K (HTR), the NbO_2 species thus formed should block surface Rh atoms to induce strong Rh–Nb_2O_5 interaction.

The diffraction pattern of the Rh metal formed by HTR of catalyst C is also anomalous in comparison with the nonpromoted Rh/SiO_2 catalyst. Only the main peak of (111) line appeared in the XRD pattern, with almost no observed diffraction corresponding to (200) and (220) lines. For the nonpromoted Rh/SiO_2 catalyst, the intensities of (200) and (220) lines were about 40 and 30% of the (111) line (*32*). Thus, we can assume that the Rh particles formed by reduction of $RhNbO_4$ exist in a needle shape oriented mainly in the ⟨111⟩ direction (*38*). The morphology change may be attributed to the strong interaction between rhodium and the niobia promoter.

After the $RhNbO_4$ compound was reduced, O_2 treatment at 773 K oxidized completely the reduced niobia species to Nb_2O_5. For the Rh particles, the surface layer is oxidized to Rh_2O_3, with the Rh core unchanged during this treatment. To obtain more precise information about the structure of this catalyst, the XRD pattern was recorded by a step-scan mode. As shown in Fig. 8, the diffraction lines of Rh_2O_3 and Rh became clear. In addition, a small peak, which can be attributed to the most intensive diffraction of the $RhNbO_4$ phase, was also observed. It suggests that some surface precursor of $RhNbO_4$ can be formed, although the O_2 treatment at 773 K is not sufficient to induce the bulk reaction between rhodium and the niobia promoter. This result is also in agreement with that obtained from TPR studies.

After the second HTR treatment at 773 K, significant SMSI effects were also observed in H_2 chemisorption and the ethane hydrogenolysis reaction. As a part of the niobia promoter would be present in the vicinity of rhodium particles, the reduction of such niobium oxide may be catalyzed by the rhodium particles. Therefore, the re-

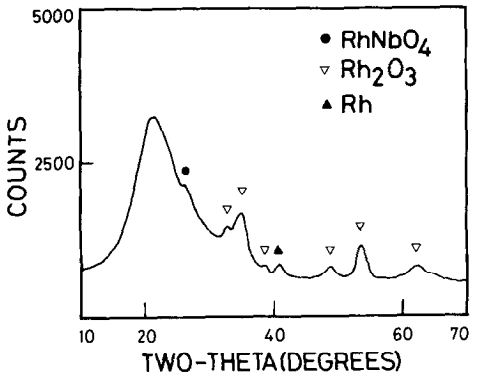

FIG. 8. X-ray diffraction pattern of catalyst C after being reduced in H_2 at 773 K and calcined in O_2 at 773 K. Step scan (step scan of 0.04°, present time of 20 s) was used.

duced niobia species can be formed from the reduction of the surface precursor of the $RhNbO_4$ compound and some of the Nb_2O_5 oxide in the vicinity of Rh particles. The formation of NbO_2 species was also confirmed by X-ray diffraction (Fig. 4, No. 5). The amount is about 0.16 in O/Rh value according to the O_2 consumption measurement. This value is significantly lower than that after the first HTR treatment. The result indicates again that the $RhNbO_4$ compound is reduced easily in comparison with the Nb_2O_5 particle, even though the reduction of a part of the latter can also be promoted by rhodium particles in the vicinity.

TPO measurements showed significant O_2 consumption at the higher temperature side after H_2 reduction either at 773 K or at 473 K (Fig. 6). However, the amount of O_2 consumption at the lower temperature side changed greatly with the reduction temperature and procedure. The amount of this peak decreases in the following order: first HTR > second HTR > H_2 reduction at 473 K. This trend is in good agreement with that obtained by the O_2 consumption measurements in a vacuum system. As most of the rhodium oxide should be reduced after H_2 reduction at 473 K, the excess amount of the O_2 consumption at the lower temperature side should thus be attributed to the oxidation of the NbO_2 species formed in the HTR treatment. It should be pointed out that two maxima (453 and 540 K) were observed in the oxidation peak at the lower temperature side, sugessting that two kinds of NbO_2 species exist in this Nb_2O_5-promoted Rh/SiO_2 catalyst system after HTR treatment. We can speculate that O_2 consumption around 453 K may be attributed to oxidation of the NbO_2 species on the Rh particles, and that the peak around 540 K may be attributed to the reduced niobia species on the support. This subject will be discussed in our next paper (*40*).

The entire results given above can be rationalized by the model in Fig. 9 which represents the structure change of the $RhNbO_4/SiO_2$ catalyst under thermal treatment in H_2 or O_2, as follows.

As the catalyst was synthesized through high-temperature calcination, the $RhNbO_4$ compound was well crystallized. The mean particle size is 139 Å according to the Scherrer formula of X-ray diffraction. The $RhNbO_4$ compound cannot be reduced in H_2 at temperatures lower than 473 K. After HTR treatment at 773 K, the $RhNbO_4$ compound was reduced to Rh and NbO_2. At the

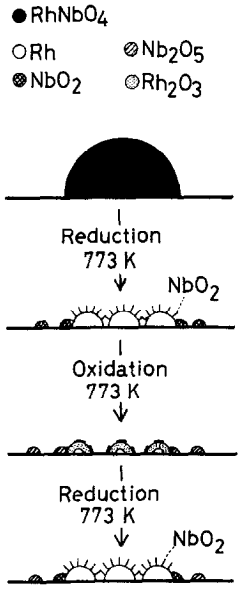

FIG. 9. Structure changes of the $RhNbO_4$ particle during treatment in H_2 or O_2.

same time, the large $RhNbO_4$ particle split into a number of smaller Rh particles. The mean size of the thus-formed Rh particles is 48 Å according to X-ray diffraction. During the following O_2 treatment at 773 K, NbO_2 is oxidized to Nb_2O_5. For the Rh particles, only the surface layer is oxidized to Rh_2O_3, with the Rh core remaining unchanged. Some surface precursor of the $RhNbO_4$ compound is also formed at the same time. After the second HTR treatment at 773 K, Rh_2O_3 and the $RhNbO_4$ precursor is reduced to form Rh particles with surfaces covered with the NbO_2 species. Some of the Nb_2O_5 promoter in the vicinity of Rh particles may also be reduced to NbO_2 during this treatment. For the two kinds of SMSI states of the Nb_2O_5-promoted Rh catalyst after the first and second HTR treatment (Fig. 9), the same extent of Rh–Nb_2O_5 interaction was observed in the H_2 chemisorption and in the ethane hydrogenolysis reaction (*39*). However, the amount of the NbO_2 species is substantially different between the two states. This means that only a restricted amount of the reduced species, as suggested by the decoration model, is necessary for the strong Rh–Nb_2O_5 interaction.

CONCLUSIONS

1. The single phase of the $RhNbO_4$ compound was formed on a silica surface through high-temperature calcination at 1173 K. This $RhNbO_4$ compound remained unchanged in H_2 at 473 K, but was reduced to Rh and NbO_2 during HTR treatment at 773 K.

2. The $RhNbO_4/SiO_2$ catalyst, once it was decomposed by HTR treatment, exhibits significant SMSI behaviors: H_2 chemisorption capacity and activity of the ethane hydrogenolysis were suppressed severely by HTR and recovered after O_2 treatment at 673 K followed by LTR treatment.

3. NbO_2 species was formed in the Nb_2O_5-promoted Rh/SiO_2 catalyst after HTR treatment. It may be this NbO_2 species which blocked the Rh surface, inducing the SMSI phenomena.

4. Rh redispersion occurred in the reduction process of the $RhNbO_4$ compound. The well-crystallized $RhNbO_4$ particle (139 Å) split into smaller Rh particles (48 Å) during HTR treatment.

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.

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