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Strong rhodium–niobia interaction in Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2 and $RhNbO_4$/SiO_2 catalysts

Application to selective CO oxidation and CO hydrogenation

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Abstract

The extent of Rh–niobia interaction in niobia-supported Rh (Rh/Nb_2O_5), niobia-promoted Rh/SiO_2 (Nb_2O_5–Rh/SiO_2) and $RhNbO_4$/SiO_2 catalyst after H_2 reduction has been investigated by H_2 and CO chemisorption measurements. These catalysts have been applied to selective CO oxidation in H_2 ($CO+H_2+O_2$) and CO hydrogenation ($CO+H_2$), and the results are compared with those of unpromoted Rh/SiO_2 catalysts. It has been found that niobia (NbO_x) increases the activity and selectivity for both the reactions. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Rh–niobia interaction; SMSI; SMOI; CO oxidation; CO hydrogenation

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1. Introduction

There has been much interest in strong metal–support interactions (SMSI) not only for metal (Rh, Pt, Pd, etc.) catalysts supported on SMSI oxides (TiO_2, Nb_2O_5, V_2O_3, MnO) but also for metal/non-SMSI oxide (SiO_2) catalysts promoted with SMSI oxides [1–4]. It is now generally accepted that a partially reduced oxide species is formed during high-temperature reduction (HTR; e.g., at 500°C), and then covers the surface of the metal particles (decoration model) [5]. The original definition of SMSI was a severe suppression of the chemisorption ability (H_2, CO) by HTR and the recovery by O_2 treatment at 400–500°C followed by low-temperature reduction (LTR) at 200–300°C. However, the effect of SMSI oxides has been observed for catalytic reactions such as CO hydrogenation even after LTR [6,7], if compared with unpromoted metal/SiO_2 catalysts. In some cases, the effect of the reduction temperature (HTR, LTR) may not be significant, because the metal surface is already covered with oxide promoters even after LTR (depending on the catalyst preparation method) [8]. So, it seems that the concept of SMSI has been expanded into the area of so called metal–oxide interactions (i.e., the effects of additives on catalysis of supported metal catalysts). Relating to SMSI, we have found calcination-induced metal–oxide interaction: mixed oxides such as $RhNbO_4$, $RhVO_4$ and Rh_2MnO_4 can be formed on an SiO_2 support by mutual interaction between Rh and oxides (vanadia, etc.) during calcination treatment in O_2 or in air of high-temperature (700–900°C) [9–12]. For instance, $RhVO_4$ is decomposed to highly dispersed Rh metal and reduced vanadium oxide (VO_x) by H_2 reduction above 200°C, and a strong metal–oxide (Rh–VO_x) interaction (SMOI) is induced on SiO_2 [11,13,14].

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Niobia (Nb_2O_5) is one of the typical SMSI oxides, and the beneficial effects of Nb on catalysis have been demonstrated [4,9,15–21]. In this work, Nb_2O_5-supported Rh (Rh/Nb_2O_5), Nb_2O_5-promoted Rh/SiO_2 (Nb_2O_5–Rh/SiO_2) and $RhNbO_4$/SiO_2 catalysts have been prepared and characterized by H_2 and CO chemisorption and X-ray diffraction (XRD) measurements, and applied to two important catalytic reactions: selective CO oxidation in H_2 ($CO+1/2O_2\rightarrow CO_2$) and hydrogenation of CO ($CO+H_2\rightarrow CH_4$, C_2H_5OH, etc.). The results are compared among the three types of rhodium–niobia catalysts (Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2, $RhNbO_4$/SiO_2) and unpromoted Rh/SiO_2 catalysts. The selective oxidation of CO in a H_2-rich atmosphere has been of considerable interest for purification of hydrogen feed gas for polymer electrolyte fuel cells (PEFCs) [22,23]. Because the chemisorption ability of H_2 and CO in these Nb catalyst system (SMSI or SMOI) is changed drastically by the calcination and/or reduction treatments, it would be interesting to investigate the $CO+H_2+O_2$ reaction [10,11,24,25]. The CO hydrogenation has also been of interest because the use of appropriate promoters (V, Nb, Mn, etc.) is essential for the improvement of the activity and selectivity. In particular, the SMSI oxides have been reported to be good promoters for the production of C_2 oxygenates such as ethanol and acetic acid [6,8,16,17,24].

2. Experimental

Two SiO_2 supports (denoted as SIO-3 and SIO-7) were provided as Japan reference catalyst (JRC) [26]. To avoid structural change during the following high-temperature calcination, these supports were calcined in air at 900°C for 3 h before impregnation of Rh and promoter (Nb, Mn) [11]. After the precalcination the BET surface area was $40\,m^2/g$ for SIO-3 and $81\,m^2/g$ for SIO-7, respectively. Nb_2O_5 support (CBMM International LTDA, AD-32) was also calcined in air at 700°C before impregnation of Rh [24]. Rh/Nb_2O_5 catalysts (0.5 wt.% Rh, 4 wt.% Rh) were prepared by impregnation of the precalcined Nb_2O_5 support (BET surface area, $40\,m^2/g$) with an aqueous solution of $RhCl_3$, then dried at 120°C overnight. After drying the Rh/Nb_2O_5 samples were calcined in air at 500°C for 1 h. Niobia-promoted Rh catalysts (Nb_2O_5–Rh/SiO_2) were prepared first by impregnation of the precalcined SiO_2 supports (SIO-3, SIO-7) with an aqueous solution of $RhCl_3$, then dried at 120°C overnight, and second by impregnation of the dried sample with $(NH_4)_3[NbO(C_2O_4)_3]$ dissolved in deionized water, and dried at 120°C overnight, then calcined in air at 500°C for 1 h [10,11]. The loading of Rh and the atomic ratio of Nb/Rh were 0.5 wt.% and 9/1 for Nb_2O_5–Rh/SIO-3, and 4 wt.% and 1/1 for Nb_2O_5–Rh/SIO-7, respectively. For a comparison, unpromoted Rh/SiO_2 catalysts (0.5 wt.% Rh/SIO-3, 4 wt.% Rh/SIO-7) were prepared by the same impregnation method using an aqueous solution of $RhCl_3$. A $RhNbO_4$/SiO_2 catalyst (4 wt.%, Nb/Rh=1/1) was prepared by the air calcination of the Nb_2O_5–Rh/SIO-7 at 900°C for 3 h [11]. A Rh_2MnO_4/SiO_2 catalyst (4 wt.%, SIO-7, Mn/Rh=1/1) was also prepared by the same impregnation method using aqueous solution of $RhCl_3$ and aqueous solution of $Mn(NO_3)_3$, then calcined in air at 900°C for 3 h [12].

The CO oxidation (50–150°C) was done in a flow reactor system at atmospheric pressure using 100 mg of the 0.5 wt.% Rh catalysts and total flow rate of $100\,cm^3/min$ (STP). The SiO_2 supports were SIO-3 except for the $RhNbO_4$/SiO_2 and Rh_2MnO_4/SiO_2. Besides, the $RhNbO_4$/SiO_2 and Rh_2MnO_4/SiO_2 catalysts were diluted by a quartz granule to adjust to the 0.5 wt.% base. The feedstream contained 3 vol.% H_2, 0.2 vol.% CO, and 1 vol.% O_2 (He balance). The CO selectivity (defined as the ratio of O_2 consumption for the CO oxidation over the total O_2 consumption) was expressed by following equation [27]:

$$S = \frac{\Delta O_{2(CO)}}{(\Delta O_{2(CO)} + \Delta O_{2(H_2)})}.$$

Before the CO oxidation measurements, the catalysts were treated in O_2 at 500°C for 1 h followed by H_2 reduction at 200 or 500°C for 1 h. The hydrogenation of CO (140–240°C) was carried out in a flow reactor system at atmospheric pressure using a 1:3 mixture of CO and H_2 ($3\,cm^3$/g-cat. min). Before the CO hydrogenation measurements, the 4 wt.% Rh catalysts (the SiO_2 supports were SIO-7) were treated in O_2 at 500°C for 1 h followed by H_2 reduction at 300 or 500°C for 1 h. For both the reactions, the pretreatments were carried out in situ, and analyses of the products were carried out by on-line gas chromatograph system equipped with TCD detector using a Porapak Q column and He as carrier gas [28].

The H_2 and CO chemisorption measurements were carried out by a conventional volumetric adsorption apparatus, and detailed procedures were described elsewhere [29]. The amounts of the total H_2 chemisorption (H/Rh) and the irreversible CO chemisorption (CO/Rh) were measured at room temperature after O_2 treatment at 500°C followed by H_2 reduction at different temperatures (200, 300, or 500°C). XRD measurements were carried out by an X-ray diffractometer (Rigaku) equipped with a graphite monochromator for Cu Kα (40 kV, 30 mA) radiation. The mean Rh particle size was calculated from the XRD line broadening measurement using the Scherrer equation [10,11,30].

3. Results and discussion

3.1. H_2 and CO chemisorption

Table 1 shows the results of the H_2 and CO chemisorption measurements for the 0.5 wt.% Rh catalysts. For the 0.5 wt.% Rh/Nb_2O_5 catalyst, the amounts of both H_2 and CO chemisorption decrease drastically after HTR at 500°C, which shows typical SMSI behavior [24]. For the Nb_2O_5–Rh/SiO_2 (SIO-3), however, the amounts of both H_2 and CO chemisorption are not so largely decreased after HTR as the Rh/Nb_2O_5 catalyst. The H/Rh and CO/Rh values after LTR at 200°C are much lower than those of the unpromoted 0.5 wt.% Rh/SiO_2 (SIO-3) catalyst, which may indicate that the metal surface is already covered with the niobia promoter. This interpretation may also be supported by the data for the 4 wt.% Rh catalysts. As shown in Table 2, the H/Rh or CO/Rh value of the Nb_2O_5–Rh/SiO_2 (SIO-7, 4 wt.% Rh) after H_2 reduction at 300°C is significantly lower than the metal dispersion (D=0.160) from XRD, which suggests that the Rh surface is covered with the niobia promoter even after LTR. The H/Rh and CO/Rh values of the 4 wt.% Rh/Nb_2O_5 catalyst are decreased drastically after HTR, which indicates the SMSI behavior. However, the chemisorption values of the Nb_2O_5–Rh/SiO_2 (SIO-7) catalyst are not so largely decreased after HTR as the 4 wt.% Rh/Nb_2O_5 catalyst. This trend is similar to that of the 0.5 wt.% Rh catalysts. For the 4 wt.% Rh/SiO_2 (SIO-7), there is no change in both H_2 and CO chemisorption values after HTR and after LTR. For the $RhNbO_4/SiO_2$, the particle size of the $RhNbO_4$ compound was 177 Å (not shown) from XRD, and the particle size of Rh metal was 64 Å (see Table 2) after the H_2 reduction at 300°C. The Rh metal is highly dispersed after the decomposition in H_2, which is in good agreement with the previous results using a different SiO_2 support [11,30]. As shown in Table 2, however, both H_2 and CO chemisorption values are severely suppressed after HTR at 500°C, in spite of the Rh particle size is not so changed. It has been already shown that the $RhNbO_4$ compound is reduced by H_2 treatment at (and above) 300°C [10,11,30], and a strong metal–oxide interaction (SMOI) is induced on SiO_2 support (see Fig. 1). As shown in Table 2, after O_2 treatment at 500°C followed by H_2 reduction at 200°C, the H/Rh value is increased from 0.010 to 0.141, but the CO/Rh value is still severely suppressed (0.010). This anomalous suppression of CO chemisorption was also observed in the previous study [25,31]. A strong Rh–niobia interaction (SMOI), including electronic, may result from H_2 reduction of the $RhNbO_4$ compound [25]. An alternative interpretation may be that CO chemisorption is suppressed by geometric blockage (decoration model) of the Rh surface even after LTR due to more intimate contact between Rh and niobia, while the H_2 uptake might be due to hydrogen spillover from Rh onto niobia and/or SiO_2 support.

Table 1
The changes in the amounts of the H_2 and CO chemisorption by the pretreatment (H_2 reduction) for the 0.5 wt.% Rh catalysts

Catalyst[a]	Reduction temperature (°C)	H/Rh	CO/Rh
0.5 wt.% Rh/Nb_2O_5	200	0.110	0.070
	500	0.000	0.010
Nb_2O_5–Rh/SiO_2[b]	200	0.060	0.047
	500	0.028	0.030
0.5 wt.% Rh/SiO_2	500	0.340	0.270

[a] The SiO_2 support is SIO-3.
[b] 0.5 wt.% Rh, Nb/Rh=9/1.

3.2. CO oxidation in the presence of H_2

Fig. 2 shows the results of oxidation reaction of H_2 (without CO) and CO (without H_2) and CO oxidation

Table 2
Comparison of Rh particle size, metal dispersion (*D*) and the amount of chemisorption after the H_2 treatment of the 4 wt.% Rh catalysts

Catalyst[a]	Reduction temperature (°C)	Particle size (Å)[b]	*D*[c]	H/Rh	CO/Rh
Rh/Nb_2O_5	300	85	0.129	0.119	0.115
	500	135	0.082	0.009	0.004
Nb_2O_5–Rh/SiO_2[d]	300	69	0.160	0.088	0.071
	500	85	0.129	0.027	0.015
$RhNbO_4/SiO_2$	200[e]	–	–	0.141	0.010
	300	64	0.172	0.031	0.001
	500	71	0.155	0.010	0.002
Rh/SiO_2	300	88	0.125	0.109	0.066
	500	101	0.109	0.113	0.068

[a] The SiO_2 support is SIO-7.

[b] From XRD measurement.

[c] Calculated from the particle size.

[d] Nb/Rh=1/1.

[e] The H_2 reduction was performed after O_2 treatment at 500°C of the $RhNbO_4/SiO_2$ catalyst which had been decomposed in H_2 at 500°C.

in the presence of H_2 for the $RhNbO_4/SiO_2$ catalyst, which was decomposed after H_2 reduction at 500°C. The activity of CO oxidation is increased slightly in the presence of H_2, while the activity of H_2 oxidation is suppressed in the presence of CO because of the saturated CO coverage of lower temperatures. It is also shown that the oxidation activity of H_2 only is lower after the HTR at 500°C than that after the O_2 treatment of the decomposed catalyst at 500°C followed by LTR at 200°C (SMSI effect). It is known that SMSI may be reversed to the normal state in the presence of O_2. In this case, however, the activity of H_2 oxidation was quite different between HTR and LTR (Fig. 2). So, it is suggested that SMSI is not reversed in the presence of O_2 with the low concentration (1 vol.%) at the low-temperatures (50–150°C). Fig. 3 compares the CO conversion (based on the same amount of Rh) for the catalysts after H_2 reduction at 500°C. The activity of CO oxidation in the presence of H_2 is as follows:

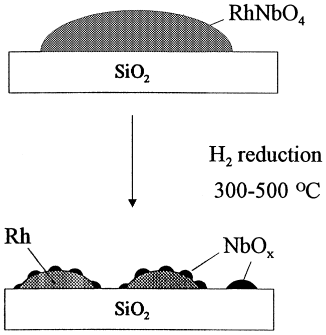

Fig. 1. A model for decomposition of $RhNbO_4$ on SiO_2 support.

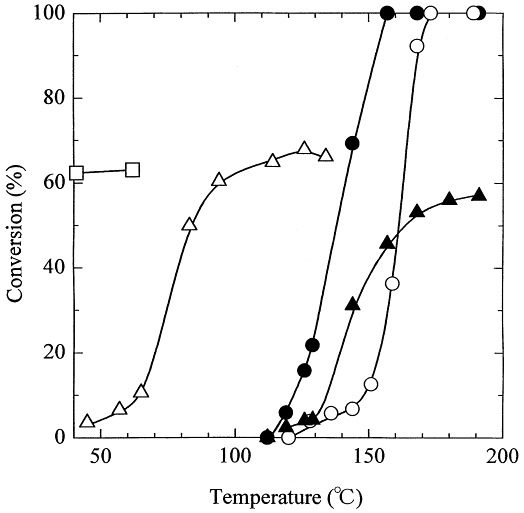

Fig. 2. Oxidation of CO and H_2 on $RhNbO_4/SiO_2$ after the decomposition by H_2 reduction at 500°C. (●) CO conversion, (▲) H_2 conversion in the feed gas of 0.2 vol.% CO, 3 vol.% H_2 and 1 vol.% O_2. (○) CO conversion in the feed gas of 0.2 vol.% CO and 1 vol.% O_2, (△) H_2 conversion in the feed gas of 3 vol.% H_2 and 1 vol.% O_2. (□) H_2 conversion in the feed gas of 3 vol.% H_2 and 1 vol.% O_2 after the O_2 treatment of the decomposed catalyst at 500°C followed by LTR at 200°C.

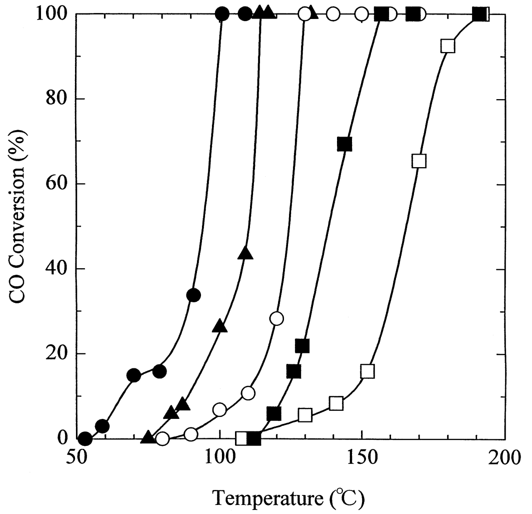

Fig. 3. Activity of CO oxidation on 0.5 wt.% Rh/Nb_2O_5, Nb_2O_5–0.5 wt.% Rh/SiO_2, $RhNbO_4/SiO_2$, Rh_2MnO_4/SiO_2 and 0.5 wt.% Rh/SiO_2 in the feedstream of 0.2 vol.% CO, 3 vol.% H_2 and 1 vol.% O_2 after H_2 reduction at 500°C. (●) Rh/Nb_2O_5, (▲) Nb_2O_5–Rh/SiO_2, (■) $RhNbO_4/SiO_2$, (□) Rh_2MnO_4/SiO_2, (○) Rh/SiO_2.

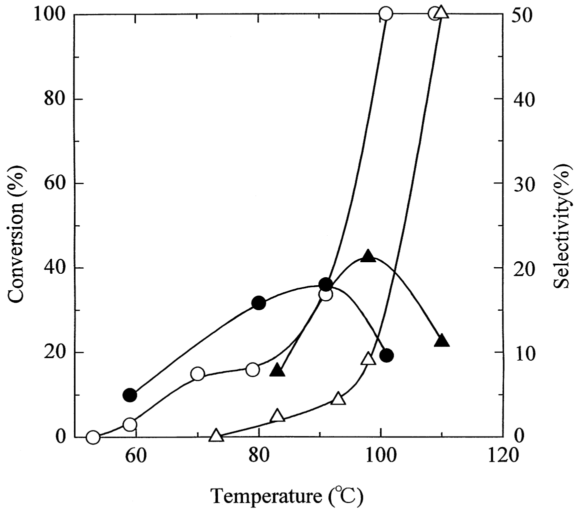

Fig. 4. Dependence of H_2 reduction temperature for the CO conversion and the CO selectivity on 0.5 wt.% Rh/Nb_2O_5 catalyst in the feedstream of 0.2 vol.% CO, 3 vol.% H_2 and 1 vol.% O_2. (○) CO conversion after HTR (H_2 500°C), (●) CO selectivity after HTR, (△) CO conversion after LTR (H_2 200°C), (▲) CO selectivity after LTR.

$Rh/Nb_2O_5 > Nb_2O_5$–$Rh/SiO_2 > Rh/SiO_2 > RhNbO_4/SiO_2 > Rh_2MnO_4/SiO_2$.

Fig. 4 shows the difference in the activity and selectivity of the 0.5 wt.% Rh/Nb_2O_5 after H_2 reduction at 200 and 500°C. The activity after HTR is higher than that after LTR in spite of the lower CO/Rh value (0.010) after HTR than that (0.070) after LTR. The CO selectivity is increased up to 20%, but finally goes down to 10%.

Fig. 5 compares the activity and selectivity between the Nb_2O_5–Rh/SiO_2 and the unpromoted Rh/SiO_2 catalysts after HTR at 500°C. The activity of the Nb_2O_5–Rh/SiO_2 is higher than that of the unpromoted Rh/SiO_2 catalyst, and the activity was also higher than that of after LTR at 200°C (not shown). The CO selectivity of the Nb_2O_5–Rh/SiO_2 is increased to 30%, which is much higher than that of the Rh/SiO_2, but finally decreases to 10%. These results suggest that the niobia in the Nb_2O_5–Rh/SiO_2 and Rh/Nb_2O_5 catalysts promotes both the activity and the selectivity under our experimental condition (CO 0.2%, O_2 1%, H_2 3%). The activity of the $RhNbO_4/SiO_2$ catalyst may be very low because of the severe suppression of CO chemisorption (Table 2). Judging from the data

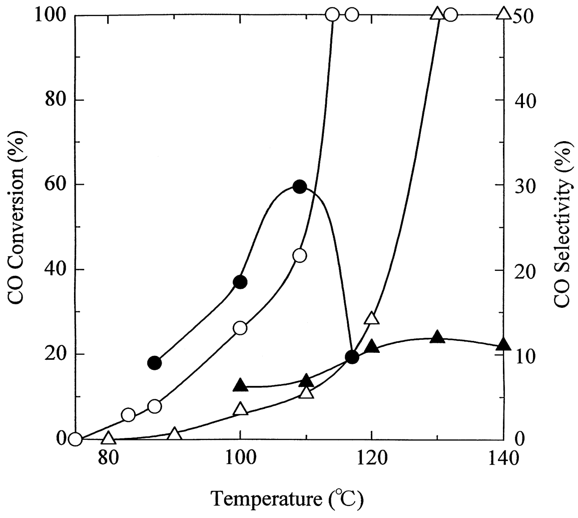

Fig. 5. Comparison of the activity and the CO selectivity for CO oxidation on Nb_2O_5–0.5 wt.% Rh/SiO_2 and 0.5 wt.% Rh/SiO_2 in the feedstream of 0.2 vol.% CO, 3 vol.% H_2 and 1 vol.% O_2 after H_2 reduction at 500°C. (○) CO conversion on Nb_2O_5–Rh/SiO_2, (●) CO selectivity on Nb_2O_5–Rh/SiO_2, (△) CO conversion on Rh/SiO_2, (▲) CO selectivity on Rh/SiO_2.

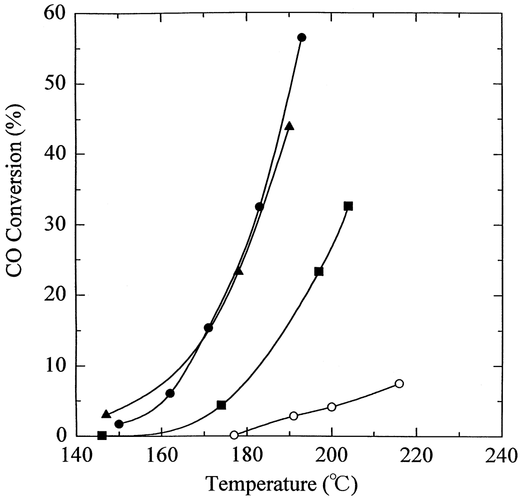

Fig. 6. Activity of CO hydrogenation over the 4 wt.% Rh catalysts (Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2, $RhNbO_4/SiO_2$ and Rh/SiO_2) after H_2 reduction at 300°C. (●) Rh/Nb_2O_5, (▲) Nb_2O_5–Rh/SiO_2, (■) $RhNbO_4/SiO_2$, (○) Rh/SiO_2.

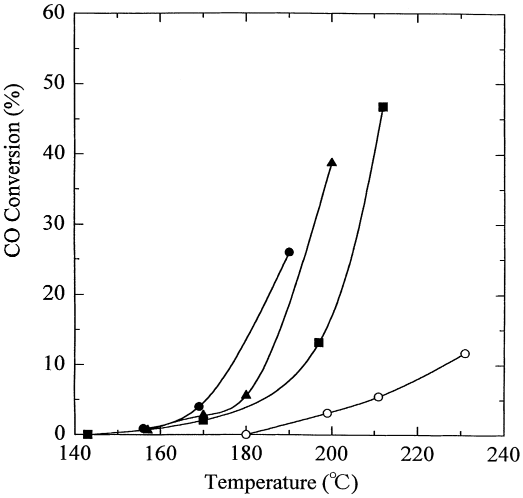

Fig. 7. Activity of CO hydrogenation over the 4 wt.% Rh catalysts (Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2, $RhNbO_4/SiO_2$ and Rh/SiO_2) after H_2 reduction at 500°C. (●) Rh/Nb_2O_5, (▲) Nb_2O_5–Rh/SiO_2, (■) $RhNbO_4/SiO_2$, (○) Rh/SiO_2.

in Table 1, however, there is no direct relationship between the chemisorption ability and the activity and selectivity.

3.3. CO hydrogenation

Fig. 6 shows the activity of CO hydrogenation over the 4 wt.% Rh catalysts after H_2 reduction at 300°C. The order of the activity is as follows: $Rh/Nb_2O_5 \cong Nb_2O_5$–$Rh/SiO_2 > RhNbO_4/SiO_2 \gg Rh/SiO_2$. For vanadia-promoted catalyst system, we have already reported that a $RhVO_4/SiO_2$ catalyst after H_2 reduction showed higher activity than V_2O_5–Rh/SiO_2 catalysts [28], and that the main promoter action of VO_x is CO dissociation [28,32]. In the niobia-promoted catalyst system, however, the activity of the $RhNbO_4/SiO_2$ is much lower than that of Nb_2O_5–Rh/SiO_2, etc. Fig. 7 shows CO conversion using the same catalysts after H_2 reduction at 500°C. The order of the activity is as follows: $Rh/Nb_2O_5 > Nb_2O_5$–$Rh/SiO_2 > RhNbO_4/SiO_2 \gg Rh/SiO_2$. Figs. 6 and 7 show that the activities of the three types of Rh–Nb catalysts (Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2, $RhNbO_4/SiO_2$) are much higher than that of the unpromoted Rh/SiO_2 catalyst. The NbO_x promoter (reduced niobia), like VO_x, may promote the activity of the CO dissociation step. The comparison between Figs. 6 and 7 reveals that the activity of each catalyst (Rh/Nb_2O_5, Nb_2O_5–Rh/SiO_2, $RhNbO_4/SiO_2$) is lower after H_2 reduction at 500°C than that after H_2 reduction at 300°C. It is recognized that the activity is decreased after the HTR because the H_2 and CO chemisorption ability is decreased after the HTR (Table 2). However, the activity of Nb_2O_5–Rh/SiO_2 is decreased more drastically after HTR at 500°C than that of Rh/Nb_2O_5, while the chemisorption ability (H/Rh, CO/Rh) of Rh/Nb_2O_5 is decreased more drastically after the HTR at 500°C than that of Nb_2O_5–Rh/SiO_2 (Table 2). Therefore, there is no strict relation between the chemisorption ability and the activity. Table 3 summarizes the catalytic results of the 4 wt.% Rh catalysts for CO hydrogenation. Because the Rh dispersion is not so much different, the TOF value based on the Rh particle size is in rough accord with the CO conversion. It should be noted that the reaction temperature for the Rh/SiO_2 is higher by 20°C in Table 3. The TOF value based on the CO chemisorption is significantly higher for the Rh/Nb_2O_5 (H_2 500°C) and the $RhNbO_4/SiO_2$ (H_2 300°C, H_2 500°C), because the CO/Rh value is severely suppressed on these catalysts. The associative chemisorption ability may not be related directly to the catalytic activity.

Table 3
Catalytic results of the 4 wt.% Rh catalysts for CO hydrogenation at 180°C (at 200°C for Rh/SiO_2) after H_2 reduction at 300°C (at 500°C in parenthesis)

Catalyst[a]	Rh/Nb_2O_5	Nb_2O_5–Rh/SiO_2	$RhNbO_4/SiO_2$	Rh/SiO_2
CO conversion (%)	27.6 (12.6)	25.5 (5.6)	8.0 (3.8)	4.2 (3.1)
TOF ($\times 10^{-4}$ s^{-1})				
(XRD)[b]	30.8 (22.0)	22.7 (6.2)	6.8 (3.7)	4.8 (4.1)
(CO/Rh)[c]	34.6 (452)	51.2 (53.1)	1165 (286)	9.0 (6.5)
Selectivity (%)				
CO_2	3.0 (4.2)	2.7 (8.4)	3.8 (5.8)	0.3 (2.2)
CH_4	37.7 (18.2)	29.5 (8.0)	3.1 (0.0)	18.1 (46.2)
C_2+[d]	23.3 (42.0)	34.0 (30.7)	43.5 (51.7)	41.7 (35.7)
MeOH	6.4 (3.0)	4.0 (7.1)	3.1 (5.5)	12.7 (4.9)
C_2 oxygenates[e]	29.6 (32.6)	29.8 (45.8)	46.5 (37.0)	27.2 (11.0)
Yield (%)				
C_2 oxygenates[e]	8.2 (4.1)	7.6 (2.6)	3.7 (1.4)	1.1 (0.3)

[a] The SiO_2 support is SIO-7.
[b] Turnover frequency based on the Rh particle size from XRD.
[c] Turnover frequency based on the CO/Rh value.
[d] Hydrocarbons containing two or more C atoms.
[e] Amount of ethanol, acetic acid, acetaldehyde and ethylene glycol.

In general, the selectivity to CH_4 tends to be higher, as the CO conversion becomes higher. However, it should be noted that for the $RhNbO_4/SiO_2$ catalyst the selectivity to CH_4 is much lower than that of the Rh/SiO_2 catalyst, in spite of the higher CO conversion of the $RhNbO_4/SiO_2$. The selectivity to C_2 oxygenates is higher for the Nb_2O_5–Rh/SiO_2 (H_2 500°C) and the $RhNbO_4/SiO_2$ (H_2 300°C) than for the unpromoted Rh/SiO_2 catalyst. However, the order of the yield of C_2 oxygenates coincides with that of the activity (CO conversion), because there is no big change in the selectivity to these catalysts.

4. Conclusions

The activity (per gram Rh) of CO oxidation in the presence of H_2 was as follows: $Rh/Nb_2O_5 > Nb_2O_5$–$Rh/SiO_2 > Rh/SiO_2 > RhNbO_4/SiO_2$. The niobia promoter affects the activity and selectivity for the CO oxidation in H_2. However, there was no direct relation between the H_2 and CO chemisorption ability and the activity and selectivity. The activity (per gram cat.; 4 wt.% Rh) of CO hydrogenation was as follows: Rh/Nb_2O_5 (H_2 300°C)$\cong Nb_2O_5$–Rh/SiO_2 (H_2 300°C)$>Rh/Nb_2O_5$ (H_2 500°C)$>RhNbO_4/SiO_2$ (H_2 300°C)$\cong Nb_2O_5$–Rh/SiO_2 (H_2 500°C)$>RhNbO_4/SiO_2$ (H_2 500°C)$\gg Rh/SiO_2$ (H_2 300°C)$\cong Rh/SiO_2$ (H_2 500°C). There is no big change in the selectivity to C_2 oxygenates, etc., but the CO conversion is increased significantly by the niobia promoter (NbO_x). So, the main promoter action of NbO_x is CO dissociation. The catalytic activity (CO dissociation) may correlate with the chemisorption ability (H/Rh, CO/Rh), although no strict relation appears to exist (e.g., Rh/Nb_2O_5 and Nb_2O_5–Rh/SiO_2 after HTR at 500°C).

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