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CO hydrogenation over a rhodium vanadate catalyst: Reduction and regeneration of $RhVO_4$ on SiO_2

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Abstract

The hydrogenation of CO over an Rh vanadate ($RhVO_4$) catalyst supported on SiO_2 ($RhVO_4/SiO_2$) has been investigated after H_2 reduction at 500°C, and the results are compared with those of vanadia-promoted (V_2O_5–Rh/SiO_2) and unpromoted Rh/SiO_2 catalysts. The mean size of Rh particles, which were dispersed by the decomposition of $RhVO_4$ after the H_2 reduction, was smaller (41 Å) than those (91–101 Å) of V_2O_5–Rh/SiO_2 and Rh/SiO_2 catalysts. The $RhVO_4/SiO_2$ catalyst showed higher activity and selectivity to C_2 oxygenates than the unpromoted Rh/SiO_2 catalyst after the H_2 pretreatment. The CO conversion of the $RhVO_4/SiO_2$ catalyst was much higher than that of V_2O_5–Rh/SiO_2 catalyst, and the yield of C_2 oxygenates increased. We also found that the $RhVO_4/SiO_2$ catalyst can be regenerated by calcination or O_2 treatment at high temperature after the reaction.

Keywords: CO hydrogenation; $RhVO_4$; SMSI; SMOI; Regeneration; Redispersion; C_2 oxygenates

1. Introduction

Vanadia-promoted Rh catalysts have been reported to have a high activity and selectivity of the syngas ($CO+H_2$) conversion for the production of C_2 oxygenates such as ethanol, acetic acid [1,2]. In both vanadia-supported and vanadia-promoted systems, it is suggested that the Rh particles are partially covered by vanadium oxide after a high-temperature reduction (so called, SMSI: strong metal–support interaction) [3–5] and that the role of the vanadium oxide promoter is to enhance the CO dissociation and/or the insertion of CO into metal–carbon bond [1,2]. We have found that a ternary compound containing rhodium, a transition metal and oxygen such as $RhNbO_4$, $RhVO_4$ and $MnRh_2O_4$ 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 at high temperature (700–900°C) [3–6]. For instance, $RhVO_4$ is decomposed to highly dispersed Rh metal and reduced vanadium oxide (VO_x) by H_2 reduction above 300°C, and a strong metal–oxide (Rh–VO_x) interaction (SMOI) is induced on SiO_2 [6–8]. One of the interesting characteristic features in this system is that regeneration of $RhVO_4$ is possible by the calcination treatment (see Fig. 1). Therefore, redispersion of Rh metal can be achieved by the calcination and reduction treatments of a spent (coked and/or sintered) Rh catalyst. The aim of this work was to investigate the catalytic performance of the $RhVO_4/SiO_2$ system for the syngas conversion and to compare the results with those of vanadia-promoted (V_2O_5–Rh/SiO_2) and unpromoted Rh/SiO_2 catalysts.

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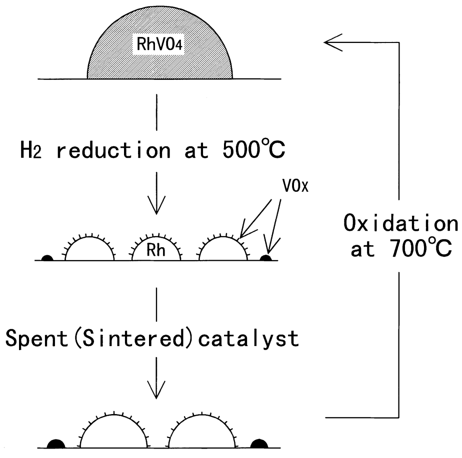

Fig. 1. A model for redispersion of Rh and regeneration of $RhVO_4$ on SiO_2 support.

2. Experimental

The SiO_2 support (JRC-SIO-7) was provided as Japan Reference Catalyst (JRC) [9]. The SiO_2 support, which had been precalcined in air at 900°C (BET surface area, 81 m^2/g), was first impregnated with an aqueous solution of $RhCl_3$ (4 wt% Rh), then dried in air at 120°C overnight. V_2O_5–Rh/SiO_2 and $RhVO_4/SiO_2$ catalysts were prepared by impregnating this sample with an aqueous solution of NH_4VO_3 (atomic ratio of V/Rh was 1 and 2, respectively), followed by calcination in air at 800°C for 3h. For a comparison, unpromoted Rh/SiO_2 catalyst was also prepared by air calcination at 800°C.

CO hydrogenation over the Rh catalysts after H_2 reduction at 500°C was carried out in a flow reactor system using mass flow controller (Nippon Tylan, Aera FC-260E) at atmospheric pressure using a 1:3 mixture of CO and H_2 (3 cm^3/g_{cat} min). For the measurement we used one sample of catalyst for increasing temperature and the steady-state reactions were established after 1 h at each temperature. Analysis of the products was performed by on-line gas chromatograph system equipped with TCD detector (Shimadzu GC-8A, Chromatopac C-R3A) using Porapak Q column (i.d. 3 mm, length 2 m) in He carrier gas (25 cm^3/min). The selectivity of products is expressed as carbon efficiency (%), and the yield (CO conversion × selectivity) of C_2 oxygenates is calculated from the total amount of C_2H_5OH, CH_3COOH, CH_3CHO and $HOCH_2CH_2OH$.

X-ray diffraction (XRD) measurements were carried out by an X-ray diffractometer (Rigaku) equipped with a graphite monochromator for Cu K_α (40 kV, 30 mA) radiation. The mean Rh particle size was calculated from the XRD line broadening measurement using the Scherrer equation [4–6].

3. Results and discussion

Fig. 2 shows XRD patterns of vanadia-promoted Rh/SiO_2 catalysts (V/Rh=1 and 2) after the calcination at 800°C. In the case of V/Rh=2, the peaks of $RhVO_4$ appeared after the calcination at 800°C. But in the case of V/Rh=1, only trace of a peak of $RhVO_4$ appeared and the other peaks were assigned to Rh_2O_3. These results of the XRD measurements indicate that $RhVO_4$ was formed on SiO_2 (SIO-7) by the calcination with an excess amount of V. Beutel et al. [13] also recently investigated the formation of $RhVO_4$ with the atomic ratio of V/Rh=4 on an SiO_2 surface. On the other hand, our previous study [6] using a different SiO_2 support (JRC-SIO-3; BET surface area, 40 m^2/g) showed that, even with the atomic ratio of V/Rh=1, $RhVO_4$ was formed almost exclusively after the calcination at 700°C. These different behaviors may be due to different natures (BET surface area, etc.) of

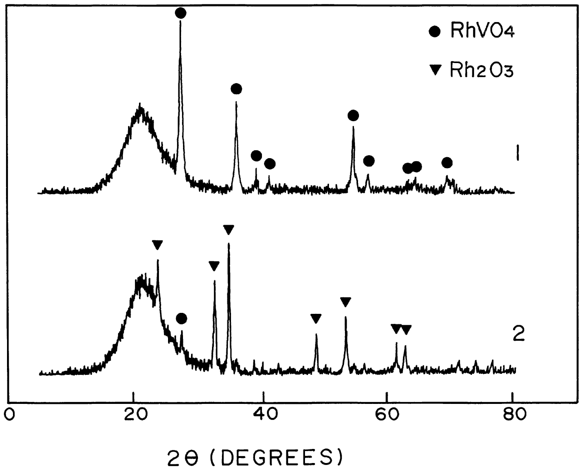

Fig. 2. X-ray diffraction patterns of $RhVO_4/SiO_2$ and V_2O_5–Rh/SiO_2 catalysts after calcination in air at 800°C: (1) V/Rh=2, and (2) V/Rh=1.

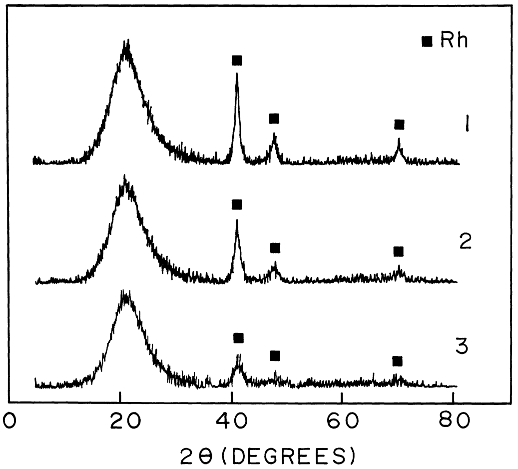

Fig. 3. X-ray diffraction patterns of $RhVO_4/SiO_2$, V_2O_5–Rh/SiO_2 and Rh/SiO_2 catalysts after H_2 reduction at 500°C: (1) Rh/SiO_2, (2) V_2O_5–Rh/SiO_2, and (3) $RhVO_4/SiO_2$.

Table 1
Particle size and catalytic activity and selectivity of vanadia-promoted and unpromoted Rh/SiO_2 catalysts

Catalyst	$RhVO_4/SiO_2$	V_2O_5–Rh/SiO_2	Rh/SiO_2
Particle size (Å)			
Compound[a]	202 ($RhVO_4$)	268 (Rh_2O_3)	229 (Rh_2O_3)
Rh[b]	41	91	101
CO conversion (%)[c]	69.7	10.6	3.8
Selectivity (%)[c]			
CO_2	22.9	10.8	8.1
CH_4	38.3	9.3	42.1
C_{2+}[d]	15.4	19.8	38.7
MeOH	5.9	4.9	5.1
C_2 oxygenates[e]	17.5	55.2	6.0
Yield (%)[c]			
C_2 oxygenates[e]	12.2	5.9	0.2

[a] After calcination in air at 800°C.
[b] After H_2 reduction at 500°C.
[c] Reaction temperature is 225°C.
[d] Hydrocarbons containing two or more C atoms.
[e] Amount of ethanol, acetic acid, acetaldehyde and ethylene glycol.

SiO_2. In fact, we have already reported different behaviors of Rh–Nb_2O_5 interaction supported on different SiO_2 supports [14]. The stronger the vanadia–SiO_2 interaction is, the more excess amount of V_2O_5 may be needed for the formation of $RhVO_4$. In practice, vanadia may be highly dispersed and/or present as isolated VO_x species in the vanadia-promoted Rh/SiO_2 catalysts (V/Rh=1 and 2), because no peak of V_2O_5 was observed in Fig. 2. Inumaru et al. [10–12] have recently reported that V-oxide is present as isolated VO_x species on SiO_2 in low V_2O_5 loading (<5 wt%), and in high V_2O_5 loading (>5 wt%) V-oxide is present as V_2O_5 particles. In this paper the catalyst with V/Rh=2 was designated as $RhVO_4/SiO_2$, and the catalyst with V/Rh=1 was designated as V_2O_5–Rh/SiO_2.

Fig. 3 shows XRD patterns of $RhVO_4/SiO_2$, V_2O_5–Rh/SiO_2 and unpromoted Rh/SiO_2 catalysts, which were calcined in air at 800°C, and then reduced in H_2 at 500°C. The peaks assigned to Rh were observed in each pattern and no peak of V-oxide was observed. Broadening of the widths of the Rh peaks was observed for the $RhVO_4/SiO_2$. Since no peak of V-oxide was observed, vanadia on SiO_2 was highly dispersed, which is in good agreement with the previous results [6,7]. As shown in Table 1, Rh was more highly dispersed (41 Å) after the decomposition of $RhVO_4$ (202 Å) by H_2 reduction at 500°C than those (91–101 Å) of V_2O_5–Rh/SiO_2 and unpromoted Rh/SiO_2 catalysts.

Fig. 4 shows CO conversion using the $RhVO_4/SiO_2$, V_2O_5–Rh/SiO_2 and unpromoted Rh/SiO_2 catalysts after H_2 reduction as a function of reaction temperature. The activity of the $RhVO_4/SiO_2$ catalyst is much higher than that of the V_2O_5–Rh/SiO_2 catalyst. The order of the activity of CO hydrogenation is as follows: $RhVO_4/SiO_2 > V_2O_5$–$Rh/SiO_2 > Rh/SiO_2$. As shown in Table 1, for the unpromoted Rh/SiO_2 catalyst CO conversion is 3.8% at 225°C. For the V_2O_5–Rh/SiO_2 catalyst CO conversion is 10.6%, and for $RhVO_4/SiO_2$ catalyst it is 69.7% at 225°C. The products are CO_2, CH_4, C_{2+} hydrocarbons, CH_3OH, and C_2 oxygenates (C_2H_5OH, CH_3COOH, CH_3CHO and $HOCH_2CH_2OH$). In the $RhVO_4/SiO_2$ catalyst a strong interaction between Rh and VO_x (SMOI) may be induced after the H_2 reduction, which may be different from that after the reduction of the V_2O_5–Rh/SiO_2. It should be noted that a metal–oxide (Rh–VO_x) interaction was also induced by the H_2 reduction of the V_2O_5–Rh/SiO_2 at 500°C, because the activity and the selectivity to C_2 oxygenates were higher than those of the unpromoted Rh/SiO_2 catalyst (Table 1). Fig. 5

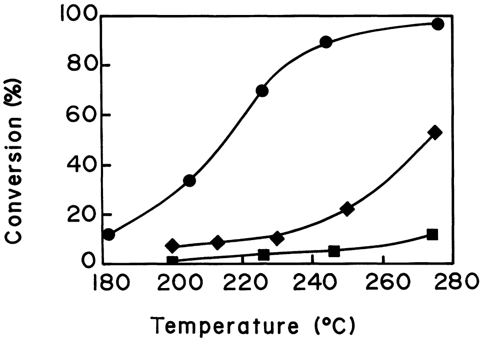

Fig. 4. The activity of CO hydrogenation on $RhVO_4/SiO_2$, V_2O_5–Rh/SiO_2 and Rh/SiO_2 catalysts after H_2 reduction at 500°C: (●) $RhVO_4/SiO_2$, (◆) V_2O_5–Rh/SiO_2, and (■) Rh/SiO_2.

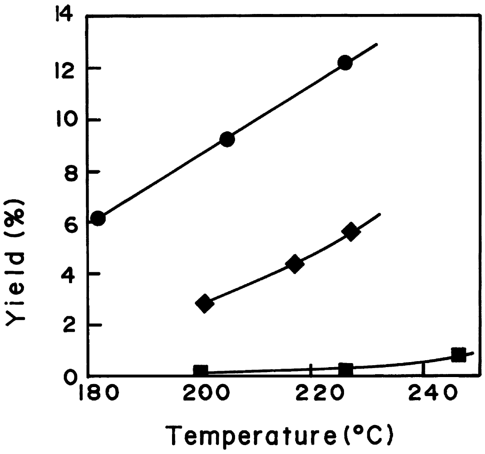

Fig. 5. The yield of C_2 oxygenates (amount of C_2H_5OH, CH_3COOH, CH_3CHO and $HOCH_2CH_2OH$) on $RhVO_4/SiO_2$, V_2O_5–Rh/SiO_2 and Rh/SiO_2 catalysts after H_2 reduction at 500°C: (●) $RhVO_4/SiO_2$, (◆) V_2O_5–Rh/SiO_2, and (■) Rh/SiO_2.

shows C_2 oxygenates yield as a function of reaction temperature. Using the unpromoted Rh/SiO_2 catalyst resulted in low yield of C_2 oxygenates, on the other hand using the $RhVO_4/SiO_2$ catalyst resulted in high yield of C_2 oxygenates. The selectivity to C_2 oxygenates decreased with increasing of CO conversion because of the secondary reactions to form CO_2 and CH_4, but the yield of C_2 oxygenates increased. These results suggest that the SMOI induced by the decomposition of $RhVO_4$ in H_2 strongly enhances the CO dissociation step, which leads to the high activity. Lee et al. [2] have reported that Rh–VO_x interaction enhances mainly CO insertion, which leads to the formation of C_2 oxygenates. On the other hand, Kip et al. [1] have reported that the main promoter action is CO dissociation. This investigation has revealed that the decomposition of the $RhVO_4/SiO_2$ catalyst enhances not only the selectivity to C_2 oxygenates (compared with the unpromoted Rh/SiO_2 catalyst), but also the CO conversion dramatically (compared with the V_2O_5–Rh/SiO_2 catalyst).

It should be noted again that the Rh particle size after the decomposition of $RhVO_4$ was 41 Å (Table 1). Arakawa et al. [15] have reported that Rh/SiO_2 catalysts, in which the size of Rh was about 30–40 Å, were most active for the formation of C_2 oxygenates. Gronchi et al. [16] have also reported that CO insertion occurred on Rh/V_2O_3, where the size of Rh was 40 Å. Therefore, we consider that the metal dispersion (Rh ensembles) may play a part in the formation of C_2 oxygenates. However, the most important point is that there is a strong Rh–VO_x interaction in the $RhVO_4/SiO_2$ catalyst system. In our $RhVO_4/SiO_2$ system, we agree with the idea [1,17] that the main promoter action of VO_x is CO dissociation. Although an Rh–VO_x interaction is also present in the V_2O_5–Rh/SiO_2 catalyst, more intimate contact between Rh and VO_x (i.e. a strong metal–oxide interaction (SMOI)) resulted from the decomposition of the $RhVO_4/SiO_2$. The SMOI increased the activity of CO hydrogenation, and hence the yield of C_2 oxygenates was increased.

In order to demonstrate the catalytic performance of the $RhVO_4/SiO_2$ system, an experiment of "regeneration of catalysts" was carried out, as shown in Fig. 6. In the initial run, CO hydrogenation was performed on a fresh $RhVO_4/SiO_2$ catalyst after H_2 reduction at 500°C. Then, the catalyst was intentionally treated in He gas at 700°C for 2 h. After the catalytic activity measurement, the catalyst was retreated in O_2 at 700°C, followed by H_2 reduction at 500°C (regeneration of $RhVO_4$ and redispersion of Rh). For a comparison, a 4 wt% Rh/SiO_2 catalyst prepared by the calcination at 500°C was used (the O_2 retreatment was also done at 500°C), because the activity of the Rh/SiO_2 prepared by the calcination at 800°C was too low to observe the change of the conversion by the He treatment. As shown in Fig. 6, the activity of the $RhVO_4/SiO_2$ catalyst was decreased severely after the He treatment, but increased to almost initial level by the calcination and reduction treatments. On the

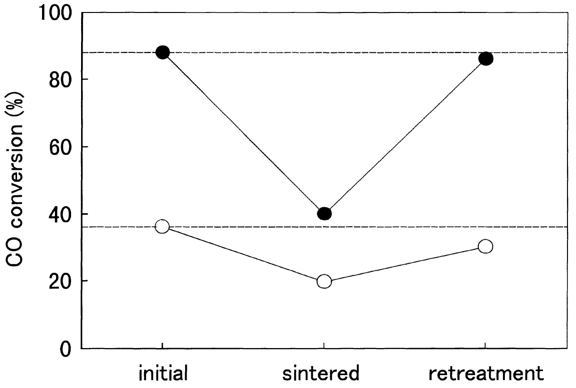

Fig. 6. The change in the activity of CO hydrogenation (245°C) on $RhVO_4/SiO_2$ (●), and Rh/SiO_2 (○) after the sequential treatments: initial (H_2 500°C), sintered (He 700°C), and retreated (O_2 700°C for $RhVO_4/SiO_2$ or O_2 500°C for Rh/SiO_2, followed by H_2 reduction at 500°C).

other hand, the recovery of the activity after the He treatment followed by O_2 and H_2 treatments at 500°C was not complete for the Rh/SiO_2 catalyst.

Acknowledgements

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