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Syngas conversion using $RhVO_4$ and Rh_2MnO_4 catalysts: Regeneration and redispersion of Rh metal by calcination and reduction treatments

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Abstract

The hydrogenation of CO over mixed oxides ($RhVO_4$, Rh_2MnO_4) supported on SiO_2 has been studied after H_2 reduction at 300°C and at 500°C, and the results compared with those of unpromoted Rh/SiO_2 catalysts. Rh was more highly dispersed (40 Å) after the decomposition of $RhVO_4$ by the H_2 reduction than those of Rh_2MnO_4/SiO_2 and unpromoted Rh/SiO_2 catalysts. The activity and the selectivity to C_2 oxygenates of the mixed-oxide catalysts after the H_2 reduction were higher than those of the unpromoted Rh/SiO_2 catalysts, but the activity of the $RhVO_4/SiO_2$ catalyst increased more dramatically after the decomposition by the H_2 reduction at 300°C, and hence the yield of C_2 oxygenates increased. These results suggest that a strong metal–oxide interaction (SMOI) was induced by the decomposition of the mixed oxides after the H_2 reduction. The catalytic activity and selectivity were reproduced repeatedly by the calcination and reduction treatments of the spent (used) catalyst because of the regeneration of $RhVO_4$ and redispersion of Rh metal.

Keywords: $RhVO_4$; Rh_2MnO_4; Mixed-oxide; CO hydrogenation; Regeneration; Redispersion; SMSI; SMOI; C_2 oxygenates

1. Introduction

The syngas ($CO+H_2$) conversion to C_2 oxygenates over Rh catalysts is a topic of great interest from both practical and mechanistic points of view. The use of appropriate supports and promoters (e.g. V, Mn, etc.) is essential for the improvement of the activity and selectivity [1,2]. For instance, vanadia-promoted and vanadia-supported Rh catalysts have been reported to have a high activity and selectivity for the production of C_2 oxygenates, such as ethanol and acetic acid [1,3], and it is suggested that the Rh particles are partially covered by partially reduced vanadium oxide (VO_x) (so-called, SMSI: strong metal–support interaction [4,5]) and that the role of VO_x is to enhance the CO dissociation and/or the insertion of CO into metal–carbon bond [1,3]. Recently, we have found that a ternary compound, containing rhodium, a transition metal and oxygen, such as $RhNbO_4$, $RhVO_4$ and Rh_2MnO_4, can be formed on an SiO_2 support by mutual interaction between Rh and the oxides (vanadia, etc.) during calcination treatment in O_2 or in air at high temperature (700–900°C) [6–8] and demonstrated that these mixed oxides play important roles not only in the catalytic properties but also in the morphology changes of the supported Rh. The characteristic features of the mixed-oxide system are as follows:

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1. Rh metal is highly dispersed after decomposition of $RhVO_4$ or Rh_2MnO_4 by H_2 reduction above 300°C;
2. a strong metal–oxide (e.g. Rh–VO_x) interaction (SMOI) is induced after the H_2 reduction [6–10];
3. regeneration of the mixed oxide by calcination treatment; and
4. redispersion of Rh metal by the H_2 reduction again.

Therefore, regeneration of catalyst can be achieved by the calcination and reduction treatments of a spent (coked and/or sintered) Rh catalyst. The present investigation was undertaken to clarify the catalytic performance of $RhVO_4$ and Rh_2MnO_4 supported on SiO_2 for the syngas conversion and to compare the results with those of unpromoted Rh/SiO_2 catalysts.

2. Experimental

The SiO_2 support (JRC-SIO-7, Japan Reference Catalyst [11]), which had been precalcined in air at 900°C (BET surface area, 81 m^2/g), was first impregnated with an aqueous solution of $RhCl_3$, then dried in air at 120°C overnight. $RhVO_4/SiO_2$ and Rh_2MnO_4/SiO_2 catalysts were prepared by impregnating this sample (4 wt% Rh) with aqueous solutions of NH_4VO_3 (atomic ratio of V/Rh=2) and $Mn(NO_3)_2$ (Mn/Rh=1), followed by calcination in air at 800° and 900°C, respectively. Unpromoted Rh/SiO_2 catalyst was also prepared by air calcination at 500° or 800°C.

CO hydrogenation over the Rh catalysts after H_2 reduction at 300° or 500°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). Analysis of the products was performed by on-line gas chromatograph system equipped with TCD detector (Shimadzu, GC-8A). X-ray diffraction (XRD) measurements were carried out by an X-ray diffractometer (Rigaku) equipped with a graphite monochromator for CuK_α (40 kV, 30 mA) radiation. The mean Rh particle size was calculated from the XRD line broadening measurement using the Scherrer equation [7].

3. Results and Discussion

The XRD measurements showed that $RhVO_4$ was formed almost exclusively on the SiO_2 support by the air calcination of the vanadia-promoted Rh/SiO_2 sample (V/Rh=2) at 800°C. The XRD patterns of $RhVO_4$ were essentially the same as those published previously [7]. As shown in Fig. 1(1), the $RhVO_4$ compound was reduced to Rh metal after the H_2 reduction at 300°C. Since no peak of V oxide was observed, vanadia (probably, VO_x) was highly dispersed, which is in good agreement with the previous results [7]. As shown in Fig. 1(2), $RhVO_4$ was reproduced after the O_2 calcination at 700°C of the used catalyst on which CO hydrogenation had been performed. Therefore, regeneration of the mixed-oxide catalyst ($RhVO_4$) was possible by the recalcination treatment, and redispersion of Rh metal can be achieved by the H_2 reduction again. In general, an excess amount of V (V/Rh=2, in this work) may be needed for the formation of $RhVO_4$. Beutel et al. [12] also recently investigated the formation of $RhNbO_4$ and $RhVO_4$ on an SiO_2 surface with V/Rh=4, and observed the calcination induced metal–promoter interaction, which is in good agreement with our previous results [7,13,14].

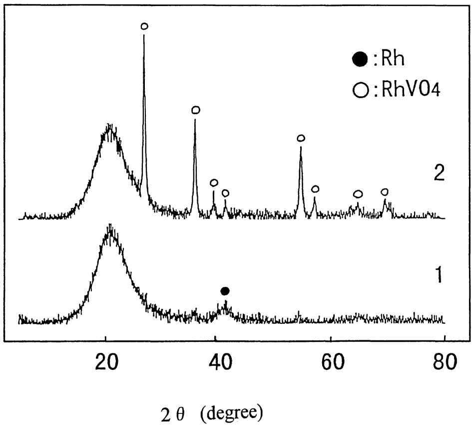

Fig. 1. X-ray diffraction patterns of a $RhVO_4/SiO_2$ catalyst (V/Rh=2): (1) after H_2 reduction at 300°C; and (2) after the CO+H_2 reaction, the catalyst was calcined in O_2 at 700°C.

Rh_2MnO_4 was formed on the SiO_2 support after the air calcination of the Rh catalyst promoted by Mn oxide at 900°C, although small peaks of the other species (Rh_2O_3) were observed in the XRD pattern (see Fig. 2(1)). As shown in Fig. 2 (2), Rh_2MnO_4 was reduced to Rh metal after the H_2 reduction at 300°C. The previous study [8] also showed that Mn oxide (MnO_x) was highly dispersed because no peak of Mn oxide was observed in the XRD pattern. As shown in

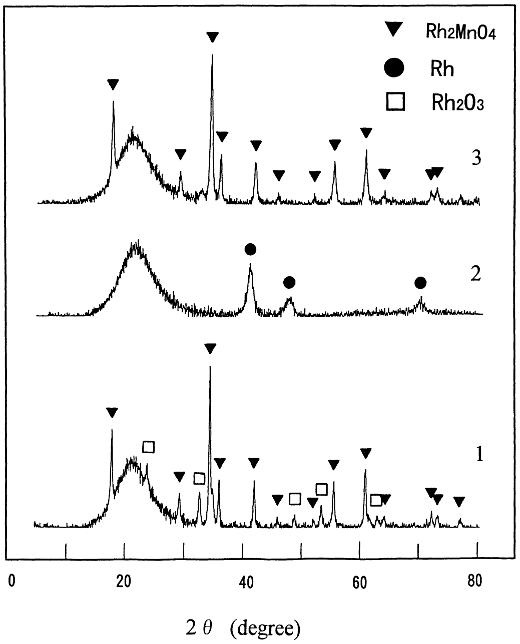

Fig. 2. X-ray diffraction patterns of a Rh_2MnO_4/SiO_2 catalyst (Mn/Rh =1): (1) as prepared by the air calcination at 900°C; (2) after H_2 reduction at 300°C; and (3) after the $CO+H_2$ reaction, the catalyst was calcined in air at 900°C.

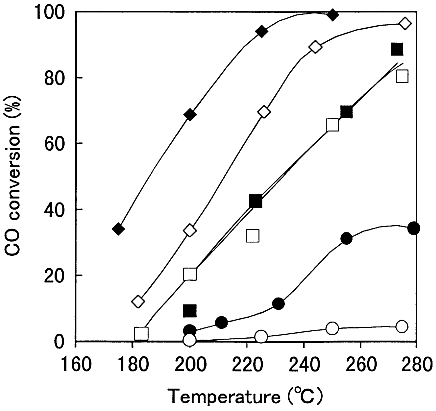

Fig. 3. The activity of CO hydrogenation: (◆) $RhVO_4/SiO_2$ after H_2 at 300°C; (◇) $RhVO_4/SiO_2$ after H_2 at 500°C; (■) Rh_2MnO_4/SiO_2 after H_2 at 300°C; (□) Rh_2MnO_4/SiO_2 after H_2 at 500°C; (●) Rh/SiO_2 (calcined at 500°C) after H_2 at 300°C; and (○) Rh/SiO_2 (calcined at 800°C) after H_2 at 500°C.

Fig. 2(3), Rh_2MnO_4 was reproduced after the air calcination at 900°C of the used catalyst on which CO hydrogenation had been performed. The important point is that the formation of the mixed oxide was much more complete (no other impurity peak) after the recalcination. This result suggests that the calcination and reduction treatments lead to more intimate contact between Rh and the promoter (MnO_x). Fig. 3 shows the activity for CO hydrogenation over $RhVO_4/SiO_2$, Rh_2MnO_4/SiO_2 and Rh/SiO_2 catalysts after H_2 reduction at 300° or 500°C. The order of the activity is as follows: $RhVO_4/SiO_2$ (calcined at 800°C)> Rh_2MnO_4/SiO_2 (calcined at 900°C)>Rh/SiO_2 (calcined at 500°C)>Rh/SiO_2 (calcined at 800°C). The activity of the $RhVO_4/SiO_2$ catalyst after the H_2 reduction at 300°C was higher than that after the H_2 reduction at 500°C, while for the Rh_2MnO_4/SiO_2 catalyst the similar activity was observed by changing the reduction temperature. Table 1 shows the particle sizes and the activities and selectivities of these catalysts. For the $RhVO_4/SiO_2$ and Rh_2MnO_4/SiO_2 catalysts the selectivity to C_2 oxygenates was higher compared with the unpromoted Rh/SiO_2 catalyst, while no significant change in the selectivity to MeOH (methanol) was observed. Fig. 4 shows the yield of C_2 oxygenates as a function of reaction temperature. The yield was much higher for the $RhVO_4/SiO_2$ catalyst than for the Rh_2MnO_4/SiO_2 catalyst at reaction temperatures between 180° and 230°C, but the yield decreased drastically at higher reaction temperatures, because the selectivity to C_2 oxygenates decreased drastically with increasing CO conversion (>90%). The secondary reactions to form

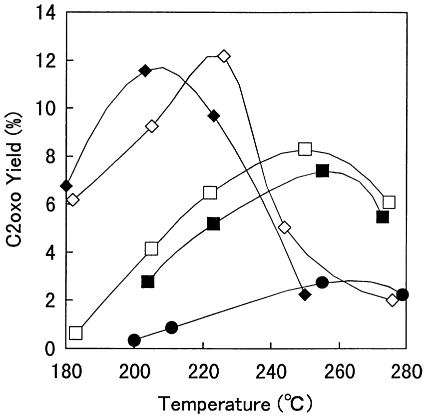

Fig. 4. The yield of C_2 oxygenates vs. reaction temperature: Key same as in Fig. 3.

Table 1
Particle sizes and CO hydrogenation over VO_x-promoted, MnO_x-promoted and unpromoted Rh/SiO_2 catalysts after H_2 reduction at 300°C (the numerals in parentheses represent the data after H_2 reduction at 500°C)

Catalyst	Rh/SiO_2	$RhVO_4/SiO_2$	Rh_2MnO_4/SiO_2
Particle size (A)			
compound	229 (Rh_2O_3) [a]	202 ($RhVO_4$) [b]	197 (Rh_2MnO_4) [c]
Rh [d]	88 (101[e])	39 (41)	69 (79)
CO Conversion (%) [f]	3.1	68.7 (33.6)	9.1 (20.2)
Selectivity (%) [f]			
CO_2	2.2	24.9 (12.0)	3.6 (3.0)
CH_4	46.2	42.6 (32.8)	31.6 (42.3)
C_2+ [g])	35.7	9.8 (23.0)	29.7 (32.3)
MeOH	4.9	5.9 (4.7)	4.7 (2.0)
C_2 oxygenates [h]	11.0	16.8 (27.5)	30.4 (20.4)
Yield (%) [f]			
C_2 oxygenates [h]	0.3	11.5 (9.2)	2.8 (4.1)

[a] Calcined in air at 500°C.
[b] Calcined in air at 800°C.
[c] Calcined in air at 900°C.
[d] After H_2 reduction at 300°C (and at 500°C).
[e] Calcined in air at 800°C followed by H_2 reduction at 500°C.
[f] At 200°C.
[g] Hydrocarbons containing two or more C atoms.
[h] Amount of ethanol, acetic acid, acetaldehyde and ethylene glycol.

CO_2 and CH_4 may occur if the CO conversion is very high.

As shown in Table 1, Rh was more highly dispersed (40 Å) after the decomposition of $RhVO_4$ by the H_2 reduction than those of the Rh_2MnO_4/SiO_2 and unpromoted Rh/SiO_2 catalysts after the H_2 reduction. Arakawa et al. [15] have reported that Rh particles in Rh/SiO_2, the size of which was ca. 30–40 Å, were most active in the formation of C_2 oxygenates. Gronchi et al. [16] have also reported that the CO insertion was enhanced 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 higher yield of C_2 oxygenates.

A more important point, however, is that there are strong metal–oxide (Rh–VO_x and Rh–MnO_x) interactions (SMOI) after the decomposition of $RhVO_4$ and Rh_2MnO_4 by H_2 reduction. We have already shown that strong Rh–VO_x and Rh–MnO_x interactions are formed by the reduction of $RhVO_4$ and Rh_2MnO_4, respectively [7,8]. For instance, the activity of ethane hydrogenolysis (which is a good test reaction to investigate the extent of metal–oxide interaction [4,5]) was decreased by 3.5 and 2 orders of magnitude after a high-temperature reduction (HTR) at 500°C of $RhVO_4$ [7] and Rh_2MnO_4 [8], respectively, compared with a low-temperature reduction (LTR) at 100°C. The nature of the strong metal–oxide (Rh–VO_x and Rh–MnO_x) interactions (SMOI) might be similar to that of SMSI (i.e. in Rh/V_2O_3 and Rh/MnO) [4,5]. In the present paper, however, we use the term SMOI, since the decomposition of the mixed oxides ($RhVO_4$, Rh_2MnO_4) on SiO_2 may result in more intimate contact between Rh and the promoter (VO_x, MnO_x).

Lee et al. [3] have reported that an 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 of VO_x is CO dissociation. The existence of an Rh–MnO_x interaction also resulted in high activity and selectivity for the production of C_2 oxygenates [17–20]. Sachtler et al. [18] have suggested that, in RhMn/NaY catalyst, only MnO particles, and not Mn^{2+} ions, promote the Rh-catalyzed formation of C_2 oxygenates. De Jong et al. [20] have shown that the activity enhancement due to MnO is only operative at modest Rh dispersions (Rh particles of size 40 Å and above). The present study showed that the decomposition of the mixed oxides ($RhVO_4$, Rh_2MnO_4) in H_2 enhances not only the selectivity to C_2 oxygenates but also the

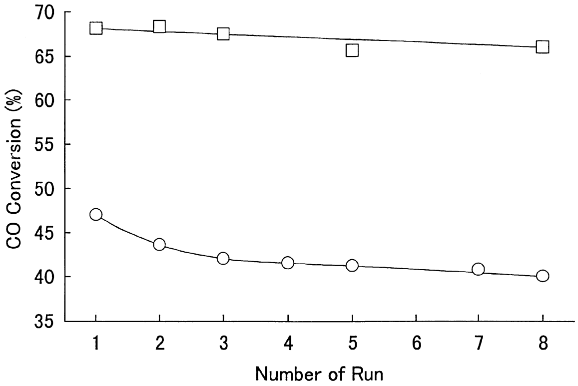

Fig. 5. CO hydrogenation at 200°C after sequential treatments (O_2 at 700°C and H_2 at 300°C): (□) $RhVO_4/SiO_2$; and (○) V_2O_5–Rh/SiO_2.

CO conversion. In particular, the Rh–VO_x interaction (SMOI) in the $RhVO_4/SiO_2$ system increased the activity dramatically and, hence, the yield of C_2 oxygenates. In relation to this work, Beutel et al. [21] have recently reported the results of CO hydrogenation at a fixed reaction temperature over Rh/V/SiO_2, Rh/Nb/SiO_2 and Rh/Ta/SiO_2 with changing calcination and reduction temperatures. They reported that high-temperature reduction favored formation of ethanol [21]. In our $RhVO_4/SiO_2$ catalyst system, however, the selectivity to C_2 oxygenates decreased significantly with decreasing reduction temperatures, because the CO conversion increased to ca. 69% (Table 1); i.e. the yield of C_2 oxygenates strongly depends on the reaction temperature (Fig. 4).

In order to demonstrate the catalytic performance of the $RhVO_4/SiO_2$ system, the activity measurements of CO hydrogenation were repeated after the sequential calcination and reduction treatments (see Fig. 5). In each run, the catalyst was treated in O_2 at 700°C, followed by H_2 reduction at 300°C, and the activity of CO hydrogenation was measured. The result was compared with a V_2O_5-promoted Rh/SiO_2 catalyst (V/Rh=1), which was calcined in air at 800°C, but no formation of $RhVO_4$ was detected by XRD. The yield of C_2 oxygenates at 200°C was 11.5% for the $RhVO_4/SiO_2$ and 7.6% for V_2O_5–Rh/SiO_2 catalyst. As shown in Fig. 5, the activity of the $RhVO_4/SiO_2$ was almost stable even after the 8th run, but the CO conversion of the V_2O_5–Rh/SiO_2 decreased gradually with repeated treatments.

Acknowledgements

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