CO hydrogenation over a $RhVO_4/SiO_2$ catalyst after H_2 reduction

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The hydrogenation of CO over a $RhVO_4/SiO_2$ catalyst has been investigated after H_2 reduction at 773 K. A strong metal–oxide interaction (SMOI) induced by the decomposition of $RhVO_4$ in H_2 enhanced not only the selectivity to C_2 oxygenates but also the CO conversion drastically, compared with an unpromoted Rh/SiO_2 catalyst. The selectivity of the $RhVO_4/SiO_2$ catalyst was similar to those of conventional V_2O_5-promoted Rh/SiO_2 catalysts (V_2O_5–Rh/SiO_2), but the CO dissociation activity (and TOF) was much higher than for V_2O_5–Rh/SiO_2, and hence the yield of C_2 oxygenates was increased.

Keywords: CO hydrogenation, high activity, SMSI, SMOI, C_2 oxygenates, $RhVO_4/SiO_2$

1. Introduction

Vanadia-promoted Rh catalysts have been reported to have a high activity and selectivity in the syngas ($CO+H_2$) conversion for the production of C_2 oxygenates such as ethanol and 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]) and that the role of the vanadium oxide promoter is to enhance the CO dissociation, which leads to a high activity, and/or the insertion of CO into the metal–carbon bond, which leads to the formation of C_2 oxygenates [1,2]. We have found a phenomenon of calcination-induced metal–promoter interaction: a mixed oxide such as $RhNbO_4$, $RhVO_4$ and $MnRh_2O_4$ can be formed on a SiO_2 support by mutual interaction between Rh and the oxide (vanadia, etc.) during calcination treatment in O_2 or in air at high temperature (973–1173 K) [3,4]. For instance, $RhVO_4$ is decomposed to highly dispersed Rh metal and reduced vanadium oxide (VO_x) by H_2 reduction above 573 K, and a strong metal–oxide (Rh–VO_x) interaction (SMOI) is induced on SiO_2 [4,5] (see figure 1). This paper reports the catalytic features of the $RhVO_4/SiO_2$ system for the syngas conversion, and the results were compared with those of vanadia-promoted (V_2O_5–Rh/SiO_2) and unpromoted Rh/SiO_2 catalysts.

2. Experimental

The SiO_2 support (JRC-SIO-7) was provided as Japan Reference Catalyst (JRC) [6]. The SiO_2 support, which had been precalcined in air at 1173 K (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 393 K overnight. V_2O_5–Rh/SiO_2 (1) and (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 1073 and 673 K, respectively) for 3 h. The $RhVO_4/SiO_2$ catalyst was prepared by calcination in air at 1073 K for 3 h after the impregnation with NH_4VO_3(aq.) (V/Rh = 2). The unpromoted Rh/SiO_2 catalyst was also prepared by air calcination at 773 K. CO hydrogenation over the Rh catalysts after H_2 reduction at 773 K 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 an on-line gas chromatograph system equipped with a TCD detector. X-ray diffraction (XRD) measurements were carried out by an X-ray diffractometer 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 [4].

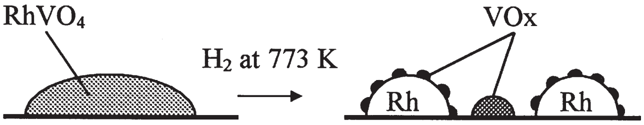

Figure 1. Decomposition of $RhVO_4$ on SiO_2 support.

3. Results and discussion

As shown in table 1, $RhVO_4$ was formed on SiO_2 (JRC-SIO-7) for the Rh catalyst (V/Rh = 2) calcined at 1073 K. For the other catalysts, $RhVO_4$ was not confirmed, but Rh_2O_3 was observed for V_2O_5–Rh/SiO_2 (1). In general, an excess amount of V (V/Rh = 2 in this work) may be needed for the formation of $RhVO_4$. The excess V oxides may be highly dispersed and/or present as isolated VO_x species on the SiO_2 support, because no peak of V oxides was observed in the XRD measurement of the $RhVO_4/SiO_2$

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Table 1
The results of CO hydrogenation at 473 K for the Rh catalysts reduced in H_2 at 773 K.

Catalyst	Rh/SiO_2	V_2O_5–Rh/SiO_2 (1)	V_2O_5–Rh/SiO_2 (2)	$RhVO_4/SiO_2$
Atomic ratio V/Rh	0	1	2	2
Calcination temp. (K)	773	1073	673	1073
XRD peaks[a]	n.d.	Rh_2O_3	n.d.	$RhVO_4$
Rh particle size[b] (nm)	10.0	9.1	6.1	4.1
CO conversion (%)	3.3	7.6	8.3	33.6
TOF[c] ($\times 10^{-4}$ s^{-1})	4.3	9.0	6.6	18.0
Selectivity[d] (%)				
CO_2	2.3	12.5	33.0	12.0
CH_4	46.9	21.6	3.5	32.8
C_{2+}[e]	34.7	22.3	25.8	23.0
MeOH	4.8	5.4	0.8	4.7
C_2 oxygenates[f]	11.3	38.2	36.9	27.5
Yield (%)				
C_2 oxygenates[f]	0.4	2.9	3.1	9.2

[a] After the calcination treatment.
[b] After H_2 reduction at 773 K.
[c] Based on the Rh particles size from XRD.
[d] Expressed as carbon efficiency (%).
[e] Amount of ethane, ethylene and C_{3+}.
[f] Amount of ethanol, acetic acid, acetaldehyde and ethylene glycol.

catalyst with V/Rh = 2. Beutel et al. [7] also recently investigated the formation of $RhVO_4$ on a SiO_2 surface with V/Rh = 4, and observed the calcination-induced metal–promoter interaction, which is in good agreement with our previous results [4]. As shown in table 1, Rh was more highly dispersed (4.1 nm) after the decomposition of $RhVO_4$ by H_2 reduction at 773 K than the Rh (6.1–10.0 nm) of the V_2O_5–Rh/SiO_2 and unpromoted Rh/SiO_2 catalysts. The order of the activity (CO conversion) after the H_2 reduction was as follows: $RhVO_4/SiO_2 > V_2O_5$–Rh/SiO_2 (2) $> V_2O_5$–Rh/SiO_2 (1) $> Rh/SiO_2$. The effect of vanadia promoter is clearly observed for the V_2O_5–Rh/SiO_2 catalysts (1) and (2), because the activity and the selectivity to C_2 oxygenates were increased significantly, compared with those of the unpromoted Rh/SiO_2 catalyst (table 1). However, the CO conversion of the $RhVO_4/SiO_2$ catalyst was much higher than those of the V_2O_5–Rh/SiO_2 catalysts. Although the same amount of vanadia promoter (V/Rh = 2) was used for the V_2O_5–Rh/SiO_2 (2), the activity (CO conversion) of $RhVO_4/SiO_2$ was much higher than that of V_2O_5–Rh/SiO_2 (2).

As shown in table 1, the TOF value of the $RhVO_4/SiO_2$ catalyst was also higher than those of the other catalysts. Therefore, the higher activity is not only due to the enhancement of Rh dispersion, but also to a strong metal–oxide (Rh–VO_x) interaction (SMOI), which is induced after the decomposition of $RhVO_4$ by the H_2 reduction. The selectivity to C_2 oxygenates of the $RhVO_4/SiO_2$ catalyst was a little lower than for the V_2O_5–Rh/SiO_2 catalysts (1) and (2) at 473 K because of a high conversion (33.6% in table 1). Because the selectivity also depends strongly on the CO conversion, the results are compared at different reaction temperatures at the condition of the same CO conversion (10%), as shown in table 2. The selectivity for the $RhVO_4/SiO_2$ catalyst was much higher than that of the unpromoted Rh/SiO_2 catalyst, but similar to (or higher than) those of the other V_2O_5-promoted Rh/SiO_2 catalysts. These results suggest that the SMOI induced by the decomposition of $RhVO_4$ in H_2 enhanced 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 catalysts). Although a Rh–VO_x interaction was also present in the V_2O_5–Rh/SiO_2 catalysts (1) and (2), more intimate contact between Rh and VO_x (i.e., SMOI) resulted from the reduction of the $RhVO_4/SiO_2$ catalyst. The SMOI increased the CO dissociation activity, and hence the yield of C_2 oxygenates was increased if compared at the same reaction temperature.

Table 2
Comparison of C_2 oxygenates production at CO conversion of 10%.

Catalyst[a]	Reaction temp. (K)	C_2 oxygenates[b] Selectivity[c] (%)	C_2 oxygenates[b] Yield (%)
Rh/SiO_2	501	17.0	1.7
V_2O_5–Rh/SiO_2 (1)	497	53.0	5.3
V_2O_5–Rh/SiO_2 (2)	488	30.0	3.0
$RhVO_4/SiO_2$	453	60.0	6.0

[a] See table 1.
[b] Amount of ethanol, acetic acid, acetaldehyde and ethylene glycol.
[c] Expressed as carbon efficiency (%).

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