Catalysis Letters 9 (1991) 331–338

PREPARATION, CHARACTERIZATION, AND CATALYTIC BEHAVIOR OF $MoRh_2O_6$ SUPPORTED ON SiO_2

K. KUNIMORI *, T. WAKASUGI, F. YAMAKAWA, H. OYANAGI,
J. NAKAMURA and T. UCHIJIMA

Institute of Materials Science, University of Tsukuba, Ibaraki 305, Japan

Received 16 January 1991; accepted 28 March 1991

Rh double-oxide compound ($MoRh_2O_6$) supported on SiO_2 was prepared by air calcination treatment of a molybdenum oxide-promoted Rh/SiO_2 catalyst at 700°C, and the chemisorptive and catalytic properties of the compound, as well as the changes in those behaviors by H_2 reduction, have been studied.

The $MoRh_2O_6/SiO_2$ catalyst exhibited almost no ability of H_2 and CO chemisorption, but a high activity for CO oxidation reaction. After H_2 treatment at 200°C, X-ray diffraction showed that the $MoRh_2O_6$ compound was reduced to a MoRh alloy, and this catalyst now exhibited a significant activity for the hydrogenolysis of cyclohexane. A drastic decrease in the activity was, however, observed after H_2 treatment at 500°C.

Keywords: Rh-Mo double oxide, rhodium molybdenum alloy, metal-oxide interaction, dehydrogenation and hydrogenolysis of cyclohexane

1. Introduction

Recently, we have found that Rh double oxides such as $RhNbO_4$ can be prepared by calcining oxide-promoted Rh/SiO_2 catalyst at high temperature (700°C–900°C) [1,2]. The $RhNbO_4/SiO_2$ catalyst exhibited a high activity for ethane hydrogenolysis reaction [2], and this catalyst system showed a strong metal-support interaction (SMSI) behavior after the $RhNbO_4$ compound was decomposed to Rh metal and NbO_2 by high-temperature reduction (HTR) at 500°C [3].

Little attention has been paid to the formation of the double oxides of noble metal such as $RhNbO_4$, $RhVO_4$ and $MoRh_2O_6$ [4,5]. The purpose of this work is to prepare such Rh double oxides on SiO_2 support, and to use these catalyst systems as starting materials to figure out chemical behaviors taking place on the SiO_2 surface during calcination and reduction treatments. We will report here the catalytic activities of cyclohexane conversion etc. and the H_2 and CO chemisorp-

---

* To whom correspondence should be addressed.

tion ability on a $MoRh_2O_6/SiO_2$ catalyst and the changes in those properties after H_2 reduction treatments. Addition of molybdena (MoO_x) to Rh/SiO_2 catalysts reportedly improves the catalytic properties for the reduction of NO by CO [6]. Formation of a bulk $MoRh_2O_6$ has been reported before [5], but no study of the reduction and catalytic behaviors of the compound has been carried out so far.

2. Experimental

The SiO_2 support (JRC-SIO-3), which had been precalcined in air at 900°C [3], was impregnated with an aqueous solution of $RhCl_3$, and sequentially with an aqueous solution of $(NH_4)_6Mo_7O_{24}$. The catalyst was dried in air at 120°C, calcined in air at 450°C for 1 h, and then kept at 700°C for 2 h in a muffle furnace. The Rh content was 5 wt%, and the loading of MoO_x was chosen so that the atomic ratio of Mo/Rh was 0.5.

The catalytic activity measurements for dehydrogenation and hydrogenolysis of cyclohexane were performed by a pulse reactor [7]. CO oxidation reaction was carried out with a conventional fixed-bed flow reactor [8]. For the H_2 and CO chemisorption measurements, the total H_2 chemisorption (H/Rh) and the irreversible CO chemisorption (CO/Rh) were measured at room temperature after H_2 reduction for 1 h at different temperatures followed by evacuation at the catalyst reduction temperature [2]. The X-ray diffraction (XRD) measurements were performed by an X-ray diffractometer (Rigaku Co. Ltd.) equipped with a graphite monochromator for Cu K_α radiation (40 kV, 30 mA) [3].

3. Results and discussion

Fig. 1 shows the XRD patterns of the MoO_x-promoted Rh/SiO_2 catalyst after the calcination and reduction treatments. The XRD pattern of the catalyst calcined at 700°C contains the new peaks attributed to a $MoRh_2O_6$ compound, and no peaks corresponding to Rh_2O_3, MoO_2, or MoO_3 were observed in fig. 1(1). As shown in table 1, the observed d spacing values and the intensities are in good agreement with those of the bulk $MoRh_2O_6$ (the tetragonal lattice parameters: $a = 4.606$ Å, $c = 3.021$ Å [5]). These results indicate that the single phase of $MoRh_2O_6$ was formed exclusively on the SiO_2 surface by the calcination treatment. As shown in fig. 1(2), almost no reduction of the $MoRh_2O_6$ compound was observed after the H_2 treatment at 100°C. However, a drastic change in the XRD pattern was observed after the H_2 reduction at 200°C (fig. 1(3)), and the new diffraction peaks became sharper after the H_2 reduction at 500°C (fig. 1(4)). table 2 shows the observed d spacing values and intensities of the new diffraction peaks. A best fit was obtained if we calculated the d values by assuming the

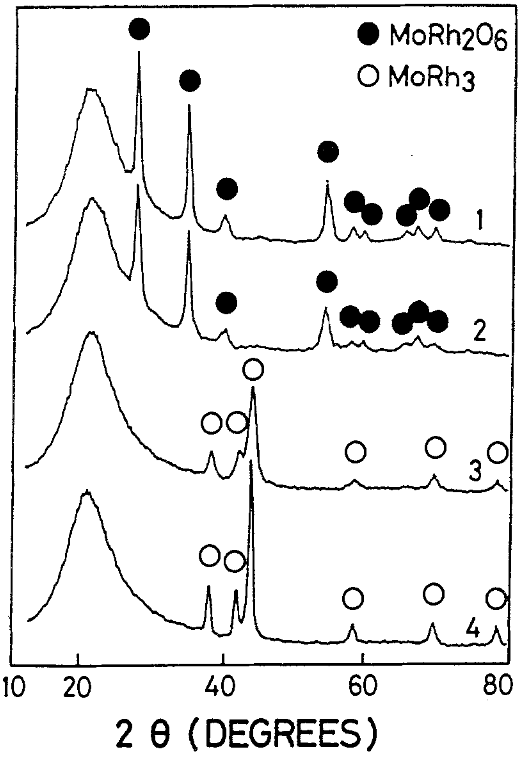

Fig. 1. X-ray diffraction patterns of MoO_x-promoted Rh/SiO_2 catalysts. (1) calcined in air at 700°C; after (1), the catalyst was treated in H_2 (2) at 100°C, (3) at 200°C, and (4) at 500°C.

hexagonal WRh_3 structure (see table 2). Therefore, it may be considered that the $MoRh_2O_6$ compound is reduced to a MoRh alloy (e.g., $MoRh_3$) by the H_2 treatment at 200°C. The mean particle sizes of $MoRh_2O_6$ and $MoRh_3$ were 14 nm

Table 1
Observed and calculated d spacing values (Å) for the new phase in fig. 1(1)

$d_{exp.}$	I/I_1	hkl	$d_{cal.}$ [a]
3.205	100	110	3.205
2.573	89	101	2.573
2.225	17	200	2.226
1.699	47	211	1.701
1.597	11	220	1.603
1.557	9	002	1.562
1.432	9	310	1.433
1.401	11	112	1.404
1.357	11	301	1.360

[a] The d spacing values were calculated by assuming that the new phase takes the tetragonal structure of bulk $MoRh_2O_6$ compound [5]. The a and c values were calculated to be 4.533 and 3.125 Å, respectively.

Table 2
Observed and calculated *d* spacing values (Å) for the new phase in fig. 1(4)

$d_{exp.}$	I/I_1	*hkl*	$d_{cal.}$ [a]
2.349	28	200	2.349
2.142	30	002	2.135
2.058	100	201	2.058
1.579	12	202	1.580
1.354	12	220	1.356
1.219	12	203	1.217

[a] The *d* spacing values were calculated by assuming that the new phase takes the hexagonal structure of WRh_3 (from the standard ASTM XRD values). The *a* and *c* values were calculated to be 5.425 and 4.269 Å, respectively.

and 8 nm, respectively, and the mean size of the MoRh alloy particles was increased to 15 nm by the H_2 treatment at 500°C, as indicated in table 3. This reduction behavior is different from that of the $RhNbO_4$ compound, which is decomposed to Rh metal and NbO_2 by the H_2 treatment at more than 300°C [2,3].

Fig. 2 shows the changes in the H_2 or CO chemisorption capacity of the $MoRh_2O_6/SiO_2$ catalyst during the sequential reduction treatments. The numbers in the figure indicate the sequential order (No.0 means that no H_2 treatment was made). The data of No.0 imply that the H_2 and CO chemisorption ability of the $MoRh_2O_6$ compound is very low. However, the chemisorption capacity was increased (No. 2) after the reduction of $MoRh_2O_6$ to the MoRh alloy, decreased by the HTR at 500°C (No. 4), and increased by the O_2 treatment at 500°C followed by low-temperature reduction (LTR) at 100°C (No. 5). In particular, the H/Rh value was increased substantially (No. 5), but decreased again by the HTR

Table 3
Changes in catalyst structure by pretreatments and CO oxidation activities of the $MoRh_2O_6/SiO_2$ and 4 wt% Rh/SiO_2 catalysts

Pretreatment	Catalyst structure	particle size [a] (nm)	Co conversion [b] (%)
Calcination at 700°C	$MoRh_2O_6$	14	13.0 [c]
H_2 500°C	$MoRh_3$	15 [d]	21.0 [e]
Calcination at 900°C	Rh_2O_3	12	1.0 [c]
H_2 500°C	Rh	13	0.3 [e]

[a] based on the XRD measurement.
[b] $W_{cat.} = 100$ mg $F = 150$ ml/min (He : O_2 : CO = 20 : 3 : 1).
[c] at 225°C.
[d] The particle size was 8 nm after the H_2 reduction at 200°C.
[e] at 115°C.

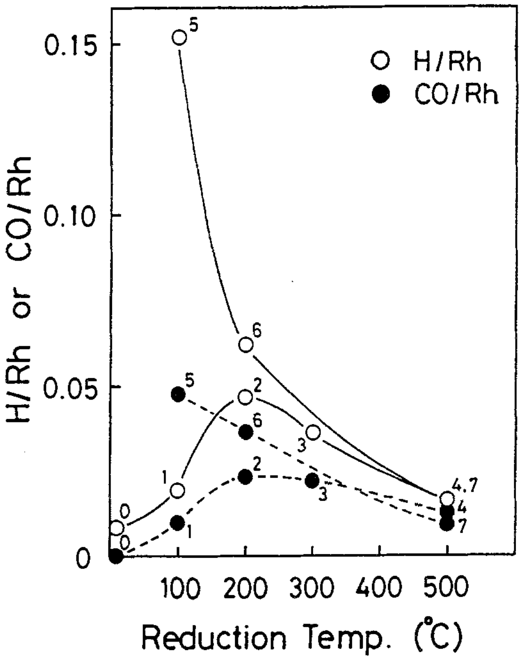

Fig. 2. Changes in the H_2 and CO chemisorption values after the sequential H_2 reduction treatments (starting material; $MoRh_2O_6/SiO_2$). The O_2 treatment at 500°C was performed before each H_2 reduction at the given temperature.

at 500°C (No. 7). These phenomena are similar to the SMSI behaviors in the $RhNbO_4/SiO_2$ [3] and Nb_2O_5-promoted Rh/SiO_2 [9] catalyst systems.

As shown in table 3, the CO oxidation activity of the $MoRh_2O_6/SiO_2$ catalyst was much higher than that of the Rh_2O_3/SiO_2 catalyst. Furthermore, the activity after the reduction of the double-oxide compound (i.e., the formation of the MoRh alloy) was also much higher than that of the unpromoted Rh catalyst after the HTR.

Fig. 3 shows the results of cyclohexane reaction over the $MoRh_2O_6/SiO_2$ catalyst after the O_2 and H_2 treatments. After the O_2 treatment at 700°C, the catalytic activity is rather high; in particular, the selectivity for hydrogenolysis is much higher than that for dehydrogenation. The hydrogenolysis activity was increased significantly by the H_2 treatment at 100°C. After the H_2 treatment at 200°C (i.e., the formation of the MoRh alloy), the catalyst has also a high hydrogenolysis activity. As shown in fig. 4, the XRD measurement of the catalyst after the catalytic activity measurement indicates that the $MoRh_2O_6$ compound was reduced to the MoRh alloy during the pulse reaction at 200°C. Therefore, the MoRh alloy may be the active species for the hydrogenolysis of cyclohexane. For comparison, the activity of the unpromoted Rh/SiO_2 catalyst is much lower than the MoRh alloy catalyst system, and there is no change in the activity and selectivity after the HTR and LTR treatments (fig. 3). Besides, molybdena

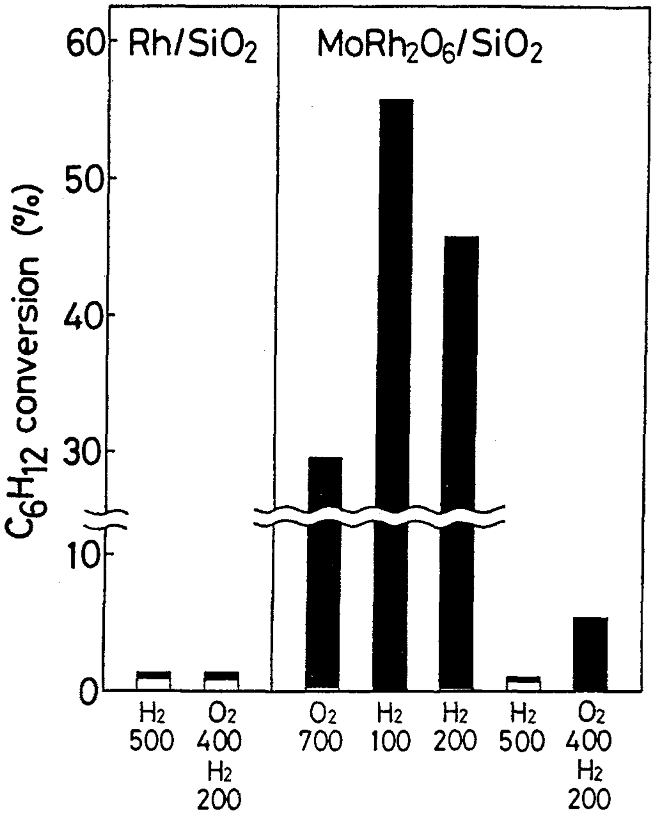

Fig. 3. The effects of the O_2 and H_2 treatments on the activities of cyclohexane reaction over the $MoRh_2O_6/SiO_2$ and 4 wt% Rh/SiO_2 catalysts (the molar H_2/C_6H_{12} ratio = 40, reaction temp. = 200°C). The O_2 treatment at 400°C was performed before each H_2 reduction at the given temperature (in °C). □: dehydrogenation (benzene formation), ■: hydrogenolysis (main product, CH_4).

supported on SiO_2 (without Rh metal) showed no activity at this reaction condition.

The hydrogenolysis activity was decreased drastically by the HTR at 500°C,

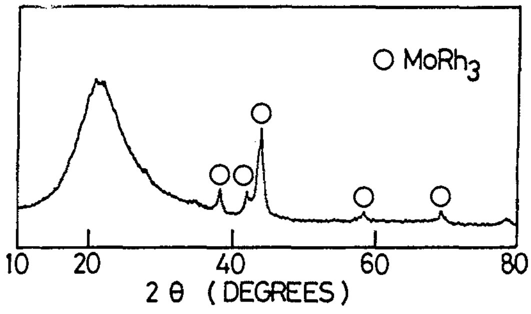

Fig. 4. X-ray diffraction pattern of the $MoRh_2O_6/SiO_2$ catalyst (which had been treated in H_2 at 100°C; i.e., at the stage No.2 in fig. 1) after the cyclohexane activity measurement (the pulse reaction at 200°C).

and increased by the O_2 treatment at 400°C followed by LTR at 200°C (fig. 3). The decrease in the activity by the HTR may be partly due to the increase of the MoRh alloy particle size (from 8 nm to 15 nm). However, it should be noted that the drastic decrease in the hydrogenolysis activity by the HTR is characteristic of the SMSI behavior [3,10]. Moreover, the chemisorption behaviors in fig. 2 are similar to those of the SMSI catalyst systems [3,9]. It appears that the catalytic properties of the MoRh alloy surface are different between the LTR and HTR treatments. More detailed characterization of the $MoRh_2O_6/SiO_2$ catalyst system will be needed to figure out the relations between the catalytic and chemisorptive properties and the catalyst surface structures.

References

[1] Z. Hu, H. Nakamura, K. Kunimori and T. Uchijima, Catal. Lett. 1 (1988) 271.
[2] K. Kunimori, H. Nakamura, Z. Hu and T. Uchijima, Appl. Catal. 53 (1989) L11.
[3] Z. Hu, H. Nakamura, K. Kunimori, Y. Yokoyama, H. Asano, M. Soma and T. Uchijima, J. Catal. 119 (1989) 33.
[4] I.S. Shaplygin, I.I. Prosychev, and V.B. Lazarev, Russ. J. Inorg. Chem. Eng. Transl. 23 (1978) 773.
[5] J. Badaud, J. Fournier and J. Omaly, C.R. Acad. Sci. Ser. C 284 (1977) 921.
[6] M.D. Wardinsky and W.C. Hecker, J. Phys. Chem. 92 (1988) 2602.
[7] Z. Hu, A. Maeda, K. Kunimori and T. Uchijima, Chem. Lett. (1986) 2079.
[8] K. Kunimori, E. Kawasaki, I. Nakajima and T. Uchijima, Appl. Catal. 22 (1986) 115.
[9] Z. Hu, H. Nakamura, K. Kunimori, H. Asano and T. Uchijima, J. Catal. 112 (1988) 478.
[10] K. Kunimori, T. Wakasugi, Z. Hu, H. Oyanagi, M. Imai, H. Asano and T. Uchijima, Catal. Lett. 7 (1990) 337.