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PREPARATION, CHARACTERIZATION, AND CATALYTIC BEHAVIOR OF Rh-Mn DOUBLE OXIDE ON SiO_2

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Rh double-oxide compound ($MnRh_2O_4$) was formed by air calcination treatment of manganese oxide-promoted Rh/SiO_2 catalyst at 900 °C, and characterized by Rietveld analysis of the X-ray diffraction pattern. The $MnRh_2O_4$ particles on SiO_2 were reduced to smaller Rh metal particles by H_2 treatment at 300 °C, and this catalyst system exhibited a strong Rh-MnO_x interaction behavior in catalytic studies of ethane hydrogenolysis and cyclohexane dehydrogenation reactions.

1. Introduction

Manganese oxide has been used as an important promoter to improve the catalytic activity and selectivity of metal catalysts (e.g., Rh/SiO_2), especially for CO hydrogenation [1]. However, further work is needed to elucidate the detailed mechanism of metal-oxide (e.g., Rh-MnO_x) interaction [2]. 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 (700–900 °C) [3,4]. The $RhNbO_4/SiO_2$ catalyst exhibits a high activity for ethane hydrogenolysis reaction, and a strong metal-support interaction (SMSI) behavior after the decomposition of the $RhNbO_4$ compound by high-temperature reduction (HTR) at 500 °C [4,5]. This work has been undertaken to study the catalytic properties of other Rh double oxides such as $RhVO_4$ and $MoRh_2O_6$ on SiO_2 surface during oxidation and reduction treatments [1].

This paper reports the structural transformation in MnO_x-promoted Rh catalysts, as well as the change in the catalytic properties, during the calcination and reduction treatments. To the best of our knowledge, the formation of Rh-Mn double oxide on SiO_2 surface has never been reported so far.

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2. Experimental

The SiO_2 support (JRC-SIO-3), which had been precalcined in air at 900 °C [5], was first impregnated with an aqueous solution of $RhCl_3$, then dried in air at 120 °C overnight. MnO_x-promoted Rh/SiO_2 catalysts were prepared by impregnating this sample with an aqueous solution of $Mn(NO_3)_2$, followed by calcination in air at 500 °C, 700 °C, or 900 °C for 3 h. The Rh content was 4 wt%, and the loading of MnO_x was chosen so that the atomic ratio of Mn/Rh was 1.0 or 0.5.

The catalytic activity measurements for ethane hydrogenolysis and cyclohexane dehydrogenation reactions were performed by a microcatalytic pulse reactor, and detailed procedures were described previously [6,7]. Before each catalytic activity measurement, the catalyst was treated in an atmospheric O_2 flow at 400 °C for 1 h, followed by reduction in an atmospheric H_2 flow at different temperatures. The X-ray diffraction (XRD) measurements were carried out by an X-ray diffractometer (Rigaku) equipped with a graphite monochromator for Cu K_α radiation (40 kV, 30 mA).

3. Results and discussion

FORMATION AND CHARACTERIZATION OF Rh-Mn DOUBLE OXIDE

Fig. 1 shows the XRD patterns of MnO_x-promoted Rh/SiO_2 catalyst (Mn/Rh = 1/1) calcined at different temperatures. After the calcination at 500 °C, the XRD pattern contains diffraction peaks of MnO_2, Rh_2O_3 and an unidentified phase probably corresponding to mixed-oxide of rhodium and manganese. The broad background peak at around 20° is due to amorphous SiO_2. After this catalyst was calcined at 700 °C, MnO_2 and the unidentified phase disappeared, and intense diffraction peaks of Rh_2O_3 were observed. In addition, a number of new diffraction peaks other than Rh_2O_3 were observed, as shown in fig. 1 (2). After the calcination at 900 °C, intensities of the new diffraction peaks increased substantially, which are assigned to those of a $MnRh_2O_4$ compound, as will be discussed later.

Fig. 2 shows the XRD patterns of MnO_x-promoted Rh/SiO_2 catalyst (Mn/Rh = 1/2). After the calcination at 700 °C, intense diffraction peaks of Rh_2O_3 were observed as shown in fig. 2 (1). As indicated by the sharp diffraction peaks, the Rh_2O_3 particles were sintered severely. Similar result is also obtained in fig. 1 (2). The mean particle size is 22 ± 2 nm according to the XRD line-broadening measurements. This size is much larger than that of unpromoted Rh_2O_3/SiO_2 catalyst, which exhibited a mean particle size of 7 nm after the calcination at 700 °C [8]. These results suggest that MnO_x promoted the agglomeration of rhodium as a result of an interaction between Rh and MnO_x.

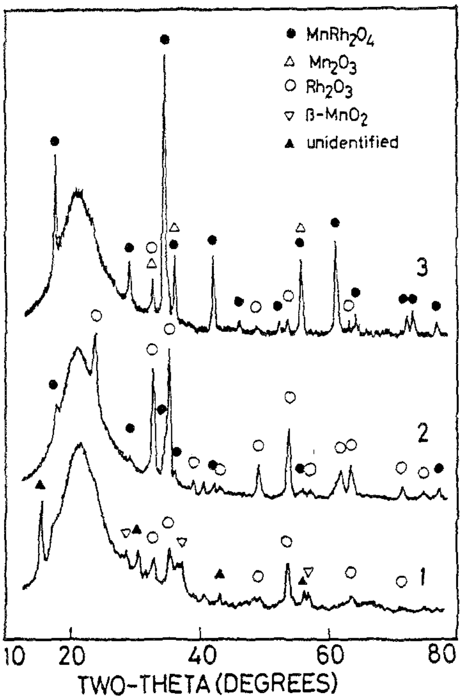

Fig. 1. X-ray diffraction patterns of MnO_x-promoted Rh/SiO_2 catalyst (Mn/Rh = 1/1) calcined in air at different temperatures; (1) 500 ° C, (2) 700 ° C, and (3) 900 ° C.

After the calcination at 900 ° C, the XRD pattern consists of the new diffraction peaks of the Rh-Mn compound ($MnRh_2O_4$), although a small contribution from Rh_2O_3 is observed, as shown in fig. 2 (2). The Rietveld analysis [5] of the

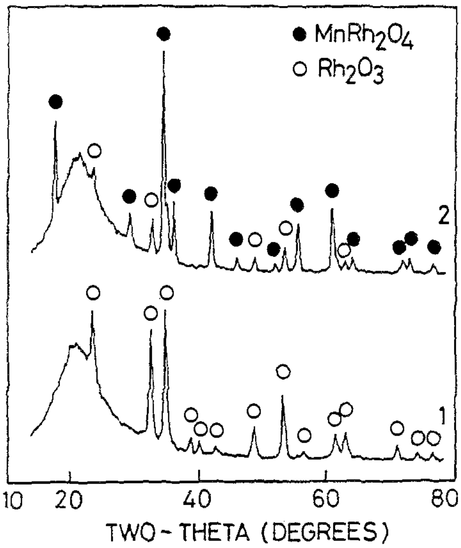

Fig. 2. X-ray diffraction patterns of MnO_x-promoted Rh/SiO_2 catalyst (Mn/Rh = 1/2); (1) calcined at 700 ° C, (2) calcined at 900 ° C.

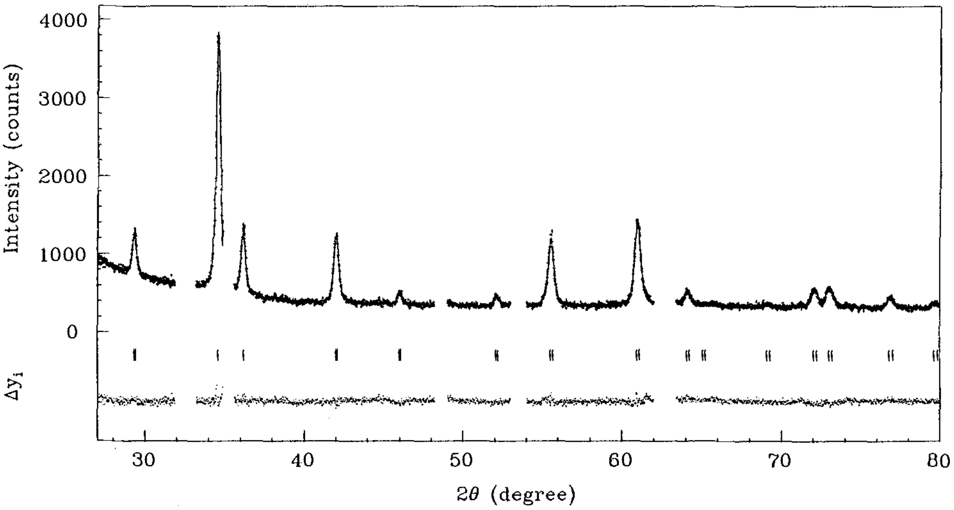

Fig. 3. Rietveld refinement pattern for the $MnRh_2O_4$ compound in the MnO_x-promoted Rh catalyst (Mn/Rh = 1/1) after being calcined at 900 °C. 2θ-regions, where diffraction peaks of Rh_2O_3 appear, are excluded in the refinement.

XRD data was carried out, as shown in fig. 3. Crosses are observed intensities, the solid line overlying them is the calculated intensity, and Δy_i is the difference between observed and calculated intensities. The short vertical lines mark the positions of possible Bragg peaks of the Rh-Mn compound. Fig. 3 shows that the calculated pattern fits the observed one well, if we assume the cubic AB_2O_4 structure (spinel; $A = Mn^{2+}$, $B = Rh^{3+}$) with the lattice parameter ($a = 0.85857$ nm). In addition, the result of refinements indicates that some disorder from the normal spinel occurs. Occupation factors of Mn in the A site and Rh in the B site are 0.89 ± 0.05 and 0.85 ± 0.04, respectively. Therefore, the chemical formula of the double oxide is $(Mn_{0.89}Rh_{0.11})(Rh_{0.85}Mn_{0.15})_2O_4$.

DECOMPOSITION OF $MnRh_2O_4$ BY H_2 TREATMENT

As shown in fig. 4, the $MnRh_2O_4/SiO_2$ catalyst (Mn/Rh = 1/2), which had been calcined at 900 °C (see fig. 2 (2)), was treated in H_2 at different temperatures. No structural change was observed by the H_2 treatment at 100 °C (No. 1), but the Rh_2O_3 phase, which is a minor constituent, was reduced to Rh metal in H_2 at 200 °C (No. 2). The decomposition of the $MnRh_2O_4$ compound was initiated by the H_2 reduction at 300 °C, where only the broad diffraction peaks corresponding to Rh metal are observed (No. 3). This result indicates that the large $MnRh_2O_4$ particles (the mean particle size of 27 ± 3 nm; see table 1) split to a number of smaller Rh particles (ca. 6 nm) during the H_2 reduction treatment (redispersion phenomenon). Similar structural transformation was also observed in the $RhNbO_4/SiO_2$ system [5]. Even after the catalyst was treated in H_2 at 500 °C (HTR), only the Rh phase (the mean particle size of ca. 12 nm; see table

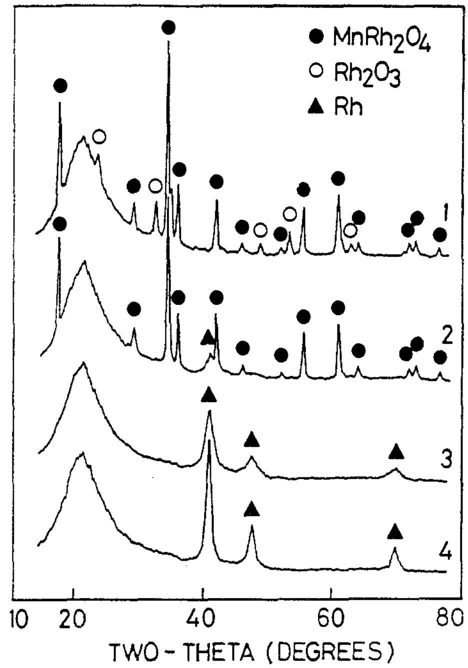

Fig. 4. X-ray diffraction patterns of the $MnRh_2O_4/SiO_2$ catalyst (Mn/Rh = 1/2) after H_2 reduction at different temperatures; (1) 100 °C, (2) 200 °C, (3) 300 °C, and (4) 500 °C.

1) was observed (No. 4). No manganese-oxide phase could be detected by X-ray diffraction, probably due to its redispersion to amorphous phase during the decomposition process.

THE CHANGES IN CATALYTIC ACTIVITIES BY H_2 TREATMENT

Table 1 shows the change in the ethane hydrogenolysis activity after the H_2 reduction treatments. It should be noted that the $MnRh_2O_4$ particles are not

Table 1
The change in the activity of ethane hydrogenolysis reaction during the sequential H_2 reduction treatments of the $MnRh_2O_4/SiO_2$ catalyst (Mn/Rh = 1/2).

Sequential treatment [a]	Catalyst structure	Particle size [b] (nm)	Activity [c]
LTR(1)	$MnRh_2O_4$	27	−5.0
LTR(2)	$MnRh_2O_4$	27	−4.0
HTR	Rh	12	−5.7
LTR(3)	Rh	7	−4.2

[a] LTR(1): H_2 100 °C; LTR(2): H_2 200 °C; HTR: H_2 500 °C; LTR(3): after HTR (i.e., after the decomposition of the compound), O_2 400 °C, H_2 100 °C.

[b] based on the XRD measurement.

[c] log rate (molecules/total Rh atom/s) at 200 °C.

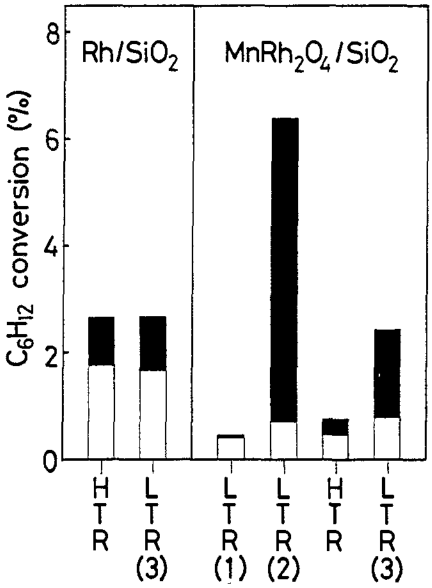

Fig. 5. The effect of the H_2 reduction treatment on the activities of cyclohexane reaction over the $MnRh_2O_4/SiO_2$ (Mn/Rh = 1/1) and 4 wt% Rh/SiO_2 catalysts calcined in air at 900 ° C (the molar H_2/C_6H_{12} ratio = 40, reaction temp. = 200 ° C). □: dehydrogenation (benzene formation), ■: hydrogenolysis (main product, CH_4), LTR(1): H_2 100 ° C, LTR(2): H_2 200 ° C, HTR: H_2 500 ° C, LTR(3): after HTR, O_2 400 ° C, H_2 200 ° C.

decomposed by the H_2 treatment at 100 ° C (LTR(1)). The data after LTR(1) imply that the activity of the $MnRh_2O_4$ compound is rather low. This result is in contrast with the case of the $RhNbO_4$ compound, which exhibited a high activity for this reaction. The increase after the H_2 treatment at 200 ° C (LTR(2)) may be due to the Rh metal phase, because the Rh_2O_3 phase was reduced by LTR(2), as shown in fig. 4 (2). The hydrogenolysis activity was decreased by ca. two orders of magnitude after the decomposition of the compound by HTR, and increased by the O_2 treatment at 400 ° C followed by H_2 reduction at 100 ° C (LTR(3)). This behavior is similar to that after the decomposition of the $RhNbO_4$ compound by HTR [4,5]. The decrease in the hydrogenolysis activity may be caused by the covering of the metal surface with MnO_x in the HTR state (the decoration model [1,2]).

Fig. 5 shows the results of cyclohexane reaction over the $MnRh_2O_4/SiO_2$ (Mn/Rh = 1/1) catalyst after the H_2 treatments. The activity of the $MnRh_2O_4$ compound after LTR(1) was very low, but increased significantly after LTR(2). In particular, the selectivity for hydrogenolysis increased drastically. As shown in fig. 6, the XRD measurement of the LTR(2) sample after the catalytic experiment suggests that the $MnRh_2O_4$ compound was reduced partly to Rh metal during the pulses of the gas mixture ($C_6H_{12} + H_2$) at the reaction condition. It should be noted that the compound was not decomposed by the treatment in H_2 at 200 ° C

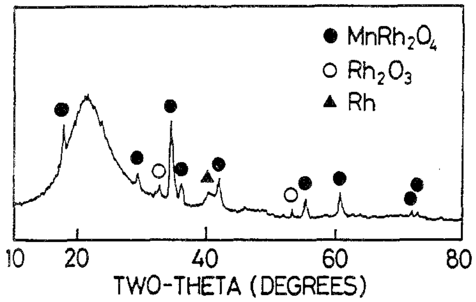

Fig. 6. X-ray diffraction pattern of the $MnRh_2O_4/SiO_2$ catalyst after the cyclohexane activity measurement (the LTR(2) sample in fig. 5).

(fig. 4), but reduced partly during the reaction at 200 °C. Although we do not have a definite explanation for this phenomenon, the presence of C_6H_{12} (and/or its fragments) may promote the reduction of the compound during the hydrogenolysis reaction.

The hydrogenolysis selectivity was decreased drastically by HTR, and increased by the O_2 treatment at 400 °C followed by LTR. For comparison, there was no change in the activity and selectivity of the unpromoted Rh/SiO_2 catalyst after the HTR and LTR treatments (fig. 5). These results show that the manganese oxide species (MnO_x) produced by the decomposition of the $MnRh_2O_4$ particles plays an important role in the catalysis on Rh metal: MnO_x appears to promote the cyclohexane hydrogenolysis reaction after LTR, but to cause the severe suppression in the activity after HTR (SMSI behavior).

Summing up, the catalytic activities of the $MnRh_2O_4$ compound are rather low, in contrast to the case of the $RhNbO_4/SiO_2$ catalyst [4]. However, a strong Rh-MnO_x interaction was induced after the decomposition of the Rh double-oxide compound as a starting material by H_2 reduction treatment: the $MnRh_2O_4$ particles are decomposed to smaller Rh metal particles (redispersion), the hydrogenolysis activities increased by LTR, and decreased significantly by HTR.

References

[1] K. Kunimori, H. Arakawa and T. Uchijima, Studies in Surface Science and Catalysis 54, in: *Future Opportunities in Catalytic and Separation Technology*, eds. M. Misono, Y. Morooka and S. Kimura (Elsevier, 1990) p. 144.
[2] G.L. Haller and D.E. Resasco, *Adv. Catal.* Vol. 36 (Academic Press, New York, 1989) p. 173.
[3] Z. Hu, H. Nakamura, K. Kunimori and T. Uchijima, Catal. Lett. 1 (1988) 271.
[4] K. Kunimori, H. Nakamura, Z. Hu and T. Uchijima, Applied Catal. 53 (1989) L11.
[5] Z. Hu, H. Nakamura, K. Kunimori, Y. Yokoyama, H. Asano, M. Soma and T. Uchijima, J. Catal. 119 (1989) 33.
[6] Z. Hu, H. Nakamura, K. Kunimori, H. Asano and T. Uchijima, J. Catal. 112 (1988) 478.
[7] Z. Hu, A. Maeda, K. Kunimori and T. Uchijima, Chem. Lett. (1986) 2079.
[8] Z. Hu, Ph.D. thesis, University of Tsukuba, 1988.